University of Aveiro Department of Materials and Ceramics Engineering

2014

Audrey Alexandra Merleau

Study of mono-firing process applied to porcelain

University of Aveiro
2014

DEPARTMENT OF MATERIALS AND CERAMICS ENGINEERING

AUDREY ALEXANDRA MERLEAU

STUDY OF MONO FIRING PROCESS APPLIED TO PORCELAIN

Thesis presented to the University of Aveiro required to obtain the Master degree of the program IMACS (International Master in Advanced Clay science). This project was produced under the scientific and technique of Prof. Paula Maria Lousada Silveirinha Vilarinho, Associate Professor of the Materials and Ceramic Engineering Department of the University of Aveiro, Dr. Paula Celeste da Silva Ferreira, Principal Researcher of the Materials and Ceramic Engineering Department of the University of Aveiro and Eng. Jorge Marinheiro, Engineer in charge of the production and research in the company PORCELANAS DA COSTA VERDE S.A.

For confidentiality reasons, it must be understood that some information concerning industrial processes cannot be communicated in this report.

Members of the Jury

Presidente: Professor Doutor Fernando Joaquim Fernandes Tavares Rocha, Professor Catedratico, Universidade de Aveiro

Vogal – Arguente Principal: Doutor Hélio Rui Caldeira da Silva Jorge, Investigador, Centro Tecnológico de Cerâmica e do Vidro de Coimbra

Vogal – Orientador: Professora Doutora Paula Maria Lousada Silveirinha Vilarinho, Professora Associada, Universidade de Aveiro

Acknowledgements

My first thanks go to my three Master’s Thesis, Professor Paula Vilarinho, Dr. Paula Ferreira and Engineer Jorge Marinheiro. I am deeply appreciative of the opportunity they offered me to realize my master thesis in an industry. I cannot thank enough Eng. J. Marinheiro for the time and the interest he gave me during the five last months. I also want to thank the company S.A. Porcelana da Costa Verde for having accepted me to work in their facilities.

I am specially grateful to my colleagues and friends Pedro and Adelino for their precious advices and their friendliness. Then, I would not forget to thank Fernando, Susana, and all my colleagues of the factory for their attention and interest they awarded me.

Special thanks go to Rui Paulo from the Mechanical Department of the University of Aveiro for his contribution to my work.

To continue, I will not forget the support and the advices given by the Professor Patricia Patrier, over the length of my Master.

I would like to express my appreciation to all the people who have contributed in some way to this report.
Finally I would like to thank my parents and my sister and my close friends for their constant support all along these two years abroad.

Audrey M.

Aveiro, 24.06.2014

Key Words Porcelain, Biscuit, Mono-firing, Bi-firing, Glaze adhesion, Microstructure.

Abstract

Porcelain production traditionally requires two main firing steps at high temperature, to get its final properties. The first firing, called biscuit firing, is realized at 1000 °C whereas the second firing, called glost firing is performed at 1380 °C. Skipping the biscuit firing represents an important saving of costs and time for porcelain companies. The cost reduction relative to the removal of the biscuit firing has been estimated at 5% of the total production cost. In addition, this industrial modification in the porcelain manufacture will also have a great environmental impact by reducing the fuel consumption.

Within this context, this study tested mono-firing process directly on the production line of Porcelanas da Costa Verde SA company. Problems encountered during mono-firing of slip casting, roller jiggering and pressed objects were identified and listed for the first time. The chosen systematic approach allows to identify the main difficulties encountered during the processing, that were mainly related with glazing and the finishing steps. Moreover, it was also verified that the number and type of defects observed on the porcelain pieces depend on the shaping process used upstream such as slip casting, roller jiggering and pressing.

When considering the glazing step, experiments clearly show that the green body absorbs less water and glaze than the biscuit. This observation was not expected and argues in favor of differences at the level of porosity and porosity distribution between the green body and the biscuit. It is proposed that although the porosity in the green body is high, it is mainly composed of very small pores. Biscuit pieces are denser due to the initial sintering stages in which the neck formation

between the grains takes place. This initial densification is enough to confer the required mechanical strength to handle the biscuit pieces.

However, though the porosity decreases after the first firing, the size of some pores may increase, forming porosity channels open up to the surface, when compared to the green pieces. This phenomenon occurs in response of the 1st sintering realized at 1000 °C. It is then suggested that this different porosity development directly impacts the difference in glaze and water absorption. The presence of the channels at the surface of the biscuit will allow a better penetration of the water and a better adhesion of the glaze. On the contrary, the small pores present in the green body do not promote this penetration of water and adhesion of glaze. Although the absence of high quality microstructures, the obtained results, that show a consistence and same trend for all the shaping processes under study, indicating that despite a high porosity the green bodies remains almost impermeable to water and glaze.

Our results clearly show that besides the weak mechanical strengthen of the green bodies, that affects directly handling and finishing steps during mono-firing, the different porosity development also contributes to the differences between mono-firing and bi-firing process of porcelain, in particular at the level of glazing. Concerning the industrial point of view, to reduce the appearance of aspect defects (cracks, bumps) during glazing, and to allow a better glaze adhesion at the surface of the green body a glazing study with glazes with different densities was conducted in the mono-fired pieces. When using a high density of the glaze suspension the final properties and appearance of mono-fired Costa Verde porcelain are very comparable to the aspect and properties of bi-fired one. The results obtained in this work though preliminary are very encouraging towards the substitution of a bi-firing cycle to a mono-firing cycle in porcelanas da Costa Verde, SA.

Contents

Index of figures and tables x

Glossary 1

Introduction 2

Objectives 3

1. Materials and methods 4

1.1. Presentation of the groups involved in the mono-firing project 4

1.2. Raw materials and porcelain pastes preparation 4

1.2.1 Liquid paste used for slip casting process 4

1.2.2 Plastic paste used for roller jiggering process 5

1.2.3 Powder paste used for pressing process 5

1.2.4 Comparison with the stoneware 6

1.3. Firing process and microstructural changes associated 8

1.4. X-ray characterization 9

1.5. Density measurements 9

1.6. SEM observations 10

1.7. Weight measurements 10

1.8. Brunauer–Emmett–Teller (BET) analysis 11

1.9. Dilatometry Analysis 12

2. Results 13

2.1. Determination of the problematic steps 13

2.1.1. Defects observed during glazing step 13

2.1.2. Defects observed during the finishing step 15

2.1.3. Automatic finishing and glazing steps 16

2.1.4. Listing of defects observed 18

2.1.5. Weight difference observed between the biscuit and the green 21

2.1.6. Glazer work 21

2.1.7. Comparison Weight % Glaze between the green and the biscuit 22

2.1.8. Difference in water absorption during the glazing step between the green and the biscuit 24

2.1.9. Glazing with different glaze densities 26

2.1.10. Observation of aesthetic aspect after glost firing for each process 29

2.2. Microstructure analysis 31

2.2.1. Mineralogical comparison between the green and the biscuit 31

2.2.2. Nitrogen adsorption results 33

2.2.3. Comparison of the green and the biscuit densities 37

2.2.4. Comparison surface porosity after glost firing 37

3. Discussion 38

3.1. Microscopic differences 38

3.2. Adaptation for improvement of mono-firing process 40

3.2.1. Warming 40

3.2.2. Transportation 40

3.2.3. Glazing 40

3.2.4 Finishing step 41

3.2.5. Automatic glazing and finishing step 41

Conclusion 42

Appendix I: Process of Porcelain Fabrication 45

Appendix II: Process paste liquid production 46

Appendix III: Process powder and plastic paste production 47

Index of figures and tables

FIGURE 1. LIQUID PAST FROM SLIP CASTING PROCESS POURED IN A GYPSUM MOLD 5
FIGURE 2. ROLLER JIGGERING - PLASTIC PASTE 5
FIGURE 3: PRESS USED TO SHAPE POWDER PASTE 6
FIGURE 4. A: PLASTIC PASTE, B: POWDER PASTE, C: LIQUID PASTE 6
FIGURE 5. TUNNEL KILN USED FOR THE GLOST FIRING 8
FIGURE 6. MICRO STRUCTURAL CHANGES: 1& 2 APPEARANCE OF GRAIN BOUNDARIES 3- INTERCONNECTED OPEN PORES BECOME ROUND 4-DECREASE OF THE POROSITY (NORTON, 1974) 9
FIGURE 7. OPERATING PROCEDURE FOR THE WEIGHT MEASUREMENT AFTER EACH STEP 11
FIGURE 8. DEFECTS OBSERVED DURING THE GLAZING STEP FOR SLIP CASTING PIECES 14
FIGURE 9. LAKE OF GLAZE DUE TO A BAD ABSORPTION OBSERVED AT THE SURFACE OF SLIP CASTING PIECES 14
FIGURE 10: IRREVERSIBLE DEFECTS OBSERVED DURING THE GLAZING OF THE PIECE PROCESSED BY ROLLER JIGGERING 15
FIGURE 11. FINISHING STEP WITH A SPONGE RUBBER DEGLAZING BELT SATURATED WITH WATER 15
FIGURE 12. PASTE REMOVAL DURING THE MANUAL FINISHING STEP (SLIP CASTING PROCESS) 16
FIGURE 13. ASPIRATION CUP FOR DISHES USED FOR AUTOMATIC GLAZING AND FINISHING. 16
FIGURE 14. DEFECTS OBSERVED BEFORE THE GLAZING AND THE FINISHING STEP (PRESSING) 17
FIGURE 15. DEFECTS OBSERVED AFTER THE AUTOMATIC FINISHING STEP (PRESSING AND ROLLER JIGGERING PROCESSED) 17
FIGURE 17. ABSORPTION OF THE GLAZE (IN WEIGHT %) WITH A DENSITY OF 1380KG/M^3 FOR PLASTIC PASTE (ROLLER) 23
FIGURE 18. ABSORPTION OF THE GLAZE (IN WEIGHT %) WITH A DENSITY OF 1380KG/M^3 FOR PRESSING 23
FIGURE 19. OPTICAL MICROGRAPHS OF THE INTERFACE BETWEEN THE CERAMIC BODY (BISCUIT, GREEN PORCELAIN AND STONEWARE) AND THE GLAZE LAYER. THE PORCELAIN GLAZE DENSITY IS1380 KG/M^3 WHILE FOR STONEWARE GLAZE THE DENSITY IS 1650 KG/M^3 24
FIGURE 20. ABSORPTION OF THE GLAZE (IN WEIGHT %) WITH DIFFERENT DENSITIES FOR GREEN WARE AND BISCUIT FOR ROLLER JIGGERING PROCESS 27
FIGURE 22. ABSORPTION OF THE GLAZE (IN WEIGHT %) WITH DIFFERENT DENSITIES FOR GREEN WARE AND BISCUIT FOR SLIP CASTING PROCESS. 28
FIGURE 23.DEFECTS OBSERVED AFTER GLOST FIRING - USE OF DIFFERENT GLAZE DENSITIES: 1350 (DENSITY NORMALLY USED IN BI-FIRED PROCESS), 1482, 1500,1550 AND 1650 (GLAZE DENSITIES USE FOR GLAZING STONEWARE). 30
FIGURE 24. XRD PATTERNS OF THE GREEN BODY, BISCUIT, THE FINAL PRODUCT OF THE MONO-FIRING PROCESS, THE FINAL PRODUCT OF THE BI-FIRING PROCESS -MINERALOGICAL CHANGE AS A FUNCTION OF THE TEMPERATURE OF FIRING 31
FIGURE 25. SEM MICROGRAPH OF THE SURFACE (NON POLISHED) OF THE GREEN WARE AND BISCUIT (SLIP CASTING) K: KAOLINITE 32
FIGURE 26. SEM MICROGRAPHS OF THE SURFACE OF THE GREEN BODY (LEFT) AND THE BISCUIT (RIGHT). 32
FIGURE 27. SEM MICROGRAPH - OBSERVATION OF THE INTERFACE GREEN/GLAZE AND BISCUIT/GLAZE 32

Figure 28. Adsorption curves for the green and the biscuit (slip casting): volume of adsorbed gas versus the gas partial pressure. ... 34
Figure 30. t-plot method to detect the microporosity of the green and the biscuit ... 34
Figure 31. Shrinkage evolution for the biscuit and the green ware. ... 35
Figure 32 . Derivative curve of the change in length versus temperature ... 36
Figure 32. Comparison surface porosity of the green fired at 1380 °C and the biscuit fired at 1000 °C and 1380 °C ... 37
Figure 33. Representation of the green body with compact arrangement ... 38
Figure 34. Representation of the biscuit fired at 1000 °C ... 39

Table 1. XRF Chemical composition of a stoneware paste and a porcelain paste processed by slip casting ... 7
Table 2. Green, biscuit, BC_BL and C_BL. identification and firing treatments of slip-casted samples. 10
Table 3: mass difference between green and biscuit (slip casting) ... 21
Table 4. Water absorbed during the glaze (wt %); slip casting process ... 25
Table 5. *Water absorbed during the glaze* (wt %); roller jiggering process ... 25
Table 6. Water absorbed during the glaze (wt %); pressing process ... 25
Table 7. Glaze densities and glaze flow values ... 26
Table 8. Density and thickness of the glaze layer absorbs at the surface of the pieces ... 28
Table 9. Observation aspect after glost firing at 1380 °C for 6h – Slip casting process ... 29
Table 10 .Observation aspect after glost firing at 1380 °C for 6h – Pressing ... 30
Table 11. Observation aspect after glost firing at 1380 °C for 6h - Roller jiggering ... 30
Table 13. Results from dilatometry analysis ... 37

Glossary

Biscuit:
Product fired once but not yet glaze.

Biscuit firing:
The process of kiln firing pottery ware before it has been glazed. In our case it corresponds to the first firing realized at 1000°C.

Glaze:
Prepared mixture which corresponds in our case to a suspension in water applied to ceramic ware by dipping.

Glazing:
Action of applying a glaze to ceramic ware unfired or in a biscuit state.

Glost firing :
The process of kiln firing ceramic after it has been glazed. In our case it corresponds to the second firing realized at 1380°C.

Green:
Ceramic ware after the shaping process but before drying and firing process.

Firing:
Process of heat treatment of tableware in a kiln.

Plastic-forming process:
Process of porcelain shaping involving roller jiggering. The paste used is plastic.

Pressing:
Process which consists in compacting and shaping a powder paste in a rigid die or flexible mold. The paste used is obtained by spray drying.

Sintering:
Process of heating a compacted powder to a temperature lower than that necessary to produce a liquid phase but important enough to cause solid-state reactions or intercrystallization. These reactions involve a strengthening of the fired body.

Specific Surface of a porous solid:
Total surface area per unit weight. The area of the internal surface of the pores is included. Units in m^2/g.

Open porosity:
It corresponds to the porosity connected to the outside.

Close Porosity:
Unlike open porosity, the pores are trapped into the material.

Introduction

In the porcelain industry the energy cost is a significant percentage of the total production cost (Agrafiotis, et al., 2001). Energy accounts for between 10 to 18 % of the total costs (Commission Européenne, 2007). Among all the different energy consuming steps, firing is the most energy intensive stage of ceramics production. Moreover, the firing processes performed in high temperature kiln and furnace consume an important quantity of fuel which contributes to the green house gas emission.

The porcelain needs to be fired at least twice for 14 and 6h, to get its final aspect, its mechanical and impermeable properties. The company COSTA VERDE realizes a first firing called **biscuit firing** at 1000 °C. The first firing is done in order to give properties (mechanical and microstructural) to the ceramic body for the next steps. The second firing step, called **glost firing** is realized at 1380 °C. The purpose of this second fire is to mature the body (total densification) and to melt the **glaze** applied to the surface of the ware to seal up the porosity and so render the ware impervious to liquid or gases. Removing one firing step could reduce considerably the production time, cost and the environmental impact (Kivitz, et al., 2009). Nowadays, mono-firing is a common technique used in stoneware tile or tableware industries. Although similar in composition, the application of fast firing process, causes many differences in terms of microstructure (Martín-Márquez, et al., 2010). The challenge of applying mono-firing to porcelain consists in avoiding (by pass) the biscuit firing without lowering the quality of the end product.

Within this context, the main objective of the present work is to identify the problems encountered in the current production line of COSTA VERDE if a mono-firing process was to be implemented. It was decided to focus this study on the slip casting process. Once the problems listed, the study was centered on identifying and understanding the differences in terms of mineralogical, phases compositions and microstructure between the green, biscuit and fired body. Results of nitrogen adsorption, water absorption, dilatometry analysis and SEM observations will be discussed. In parallel, green bodies of each process were glaze with different glaze densities. The results will be described and discussed.

To finish, the estimated cost of mono-fired porcelain will be compared to the cost of the bi-fired product.

Objectives

- The first objective of my work was to identify, directly on the production line of the company Costa Verde, the main steps where problems are encountered.

- Once these steps identified, the second stage of my work was to list all the defects observed for each problematic step and each process.

- The following part of my study was to give an explanation for this problem by comparing the microstructure of the biscuit and the green body.

- Finally, the last step was to propose solutions, for some of the problems encountered, to get around the issues to improve the mono-firing results.

1. Materials and methods

1.1. Presentation of the groups involved in the mono-firing project

This study has been done within the company COSTA VERDE. This industry, located in Vagos, close to Aveiro in Portugal, began its activity in 1992. Today, they produce and export tableware porcelain all around the world. Most of the samples were prepared and the experiments realized directly with the raw materials and on the production line of the company.

Department of Materials and Ceramics Engineering of the University of Aveiro was also involved in this project, supporting mainly the structural and microscopic analysis of the materials.

1.2. Raw materials and porcelain pastes preparation

The first step in porcelain production consists in the paste preparation. COSTA VERDE produces two different pastes used for three different processes; slip casting, roller jiggering and pressing.

1.2.1 Liquid paste used for slip casting process

Liquid past is an industrial porcelain slurry, used for **slip casting**, and made mainly from kaolin feldspar and quartz. Feldspars, quartz and English clays are stirred up with water and crushed together in an industrial ball mill for different laps of time depending of the granulometry of the initial material. After this process, kaolins are added to the slurry and the paste undergoes a sieving and an iron removing. Indeed, iron particles cause yellowing of the paste during firing and should be avoided. The resulting liquid slurry is then used for three different castings; handles, high pressure and manual slip casting. The particularity of manual slip casting method is that it needs intensive labor thus making it more costly at a large-scale production. Once the paste is ready, it will be poured into a gypsum or resin mold (*Figure 1*).

Figure 1. Liquid past from slip casting process poured in a gypsum mold

1.2.2 Plastic paste used for roller jiggering process

The plastic pastes are also made from quartz sand, feldspars, and Kaolin but in different proportions. As the preparation of the liquid paste, feldspars, quartz and English clays are stirred up with water and crushed together in an industrial ball mill. Then kaolin, thin enough not to be grinded, is added to the mixture. After homogenization and iron removal from the slurry, the plastic paste is filtered, pressed and extruded. Extrusion process is used in order to produce a de-aired plastic feed material of controlled volume (long cylinders Figure 4-A). The material once shaped into cylinders is used in jiggering operation (*Figure 2*).

Figure 2. Roller jiggering - plastic paste

1.2.3 Powder paste used for pressing process

The composition of the powder paste is the same than the one used to make the plastic paste. However, the process to produce it is different. The liquid slurry is first filtered and mixed with deflocculant. The mixture obtained is called Barbotine. The later is dried in a spray dryer at high temperature (around 300 °C). The powder obtained is composed of a multitude of small balls (Figure 4-B). This powder is then poured in a press. Inside the latter the pressure applied reaches 200 to 350 bars.

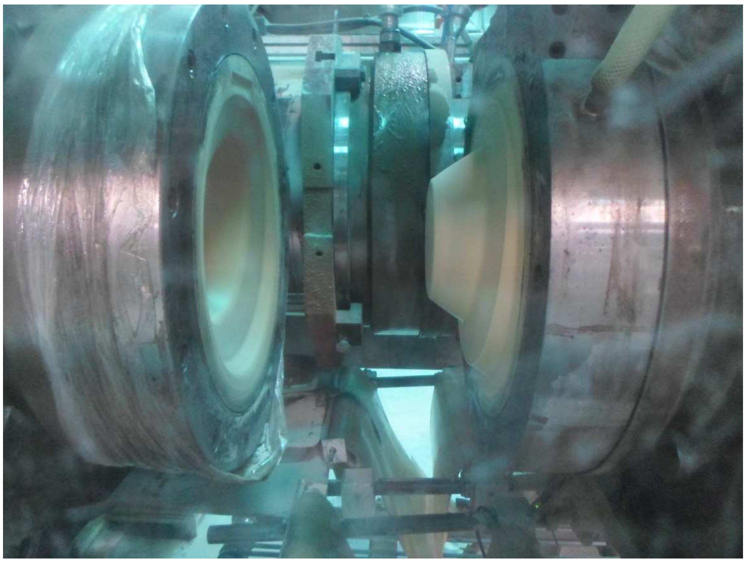


Figure 3: Press used to shape powder paste

Entire process of porcelain production is described Appendix I.

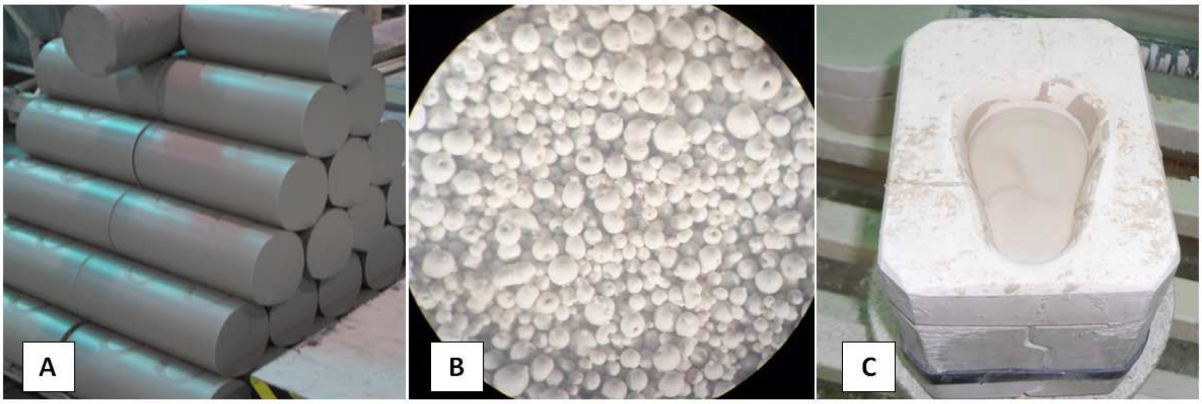


Figure 4. A: plastic paste, B: powder paste, C: liquid paste

1.2.4 Comparison with the stoneware

Stoneware is commonly mono-fired. For this reason, the green material was compared with the green porcelain body.

Stoneware used in this study as a comparison step, was provided by the company GRESTEL. It has also a triaxial ceramic composition although the quantity of quartz, kaolinite and feldspars are different from the ones used in the porcelain composition. The mineral composition in weight percent was not provided by the industry because unlike COSTA VERDE, the stoneware company does not produce the paste. However in the literature, standard stoneware composition consists in 45-50% of kaolinite, 35-45% feldspars and 10-15% of quartz sand (Martín-Márquez, et al., 2010). The density of the glaze used to enamel the porcelain is normally in between 1380 - 1390 kg/m3 whereas the density of the glaze applied on stoneware is higher, around 1640 -1650 kg/m3.

The chemical compositions of the two pastes, obtain from X-Rays fluorescence analysis, are given Table 1.

Table 1. XRF Chemical composition of a stoneware paste and a porcelain paste processed by slip casting

	stoneware	*green porcelain slip casting process*
	(%)	(%)
LOI (Loss in ignition)	6.15	8.48
SiO_2	64.885	60.472
Al_2O_3	25.022	27.82
K_2O	1.29	1.76
Na_2O	0.817	0.355
MgO	0.335	0.133
Fe_2O_3	0.628	0.588
CaO	0.172	0.098
P_2O_5	0.203	0.102
SO_3	0.063	0.061
TiO_2	0.285	0.062

Each mineral plays a specific role. Clays act as binder for the other constituents in the green state, confers plasticity on the body for shaping and is usually kaolinite. Indirectly it also enhances the mechanical properties of the porcelain. Indeed, kaolinite when fired above 550°C turns first into metakaolinite by removing the hydroxyl groups following the reaction $Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O$ then, at about 1000 °C the formation of mullite begins. This mineral is known as specie which improves the strength of the porcelain (Martín-Márquez, et al., 2010). Feldspars are used as flux. They facilitate the appearance of a liquid phase because they melt at low temperatures. Moreover, they improve the densification of the ceramic body by filling the pores. To finish, quartz addition is an indispensable part of the paste preparation, indeed it reduces deformation and shrinkage during the firing.

In

Table ***1***, SiO2 enters in quartz, kaolinite and feldspars composition. Aluminum oxide comes mainly from kaolinite and a little bit in feldspars. And potassium and sodium oxides come mainly from feldspars. The stoneware contains more flux than the porcelain paste.

According to XRD analysis, glaze is composed of microcline (feldspar), calcite, gibbsite, dolomite and quartz.

1.3. Firing process and microstructural changes associated

Green ware contains between 25 and 50 volume percent of porosity (depending on forming method, particle size and distribution). This porosity is removed after the complete firing process and is linked to the volume firing shrinkage.

The biscuit and glost firing applied on all the samples were realized directly with the industrial tunnel kiln (Figure 5).

Figure 5. Tunnel kiln used for the glost firing

Biscuit firing lasts 32 h including the drying cycle at a maximum temperature of 1000 °C. The temperature used for the first sintering is well below the temperature of melting. The main purpose is related to the creation and growth of contacts between grains. At the end of this step, each object has been hardened and the density is around 1.5g.cm^{-3}; the microstructure reveals a network of open porosity. The second firing is shorter and lasts 6 h at a maximum temperature of 1380 °C. During this step the densification takes place with the help of the liquid phase that appears after ~1100C and the grains grow. This step results in consolidation and decreasing of volume.

Many micro structural changes occur during the stages of solid-state sintering. In the initial step, surfaces of the particles become smooth, grain boundaries appear, interconnected open pores become round and the porosity decreases slightly (Figure 6). During intermediary stage, open pores intersecting grain boundaries, shrink the porosity average decreases significantly and grains growth slowly.

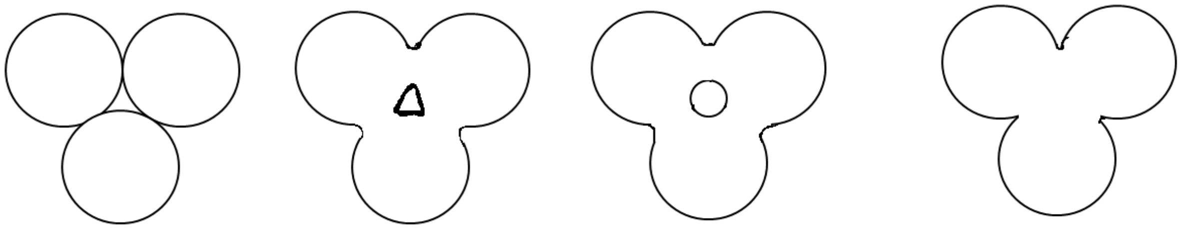


Figure 6. Micro structural changes: 1& 2 appearance of grain boundaries 3- interconnected open pores become round 4-decrease of the porosity **(Norton, 1974)**

Unlike porcelain, industrial stoneware undergoes only one fast firing process. This difference is known as being one of the reason for microstructures differences between the two products after firing.

1.4. X-ray characterization

Crystalline phase identification was performed on powder prepared from liquid and plastic porcelain pastes and stoneware collecting at different steps of the production using a X-ray diffractometer (Rigaku) operating with Cu Kα= 1.54056A˚ radiation. The detail of the sampling is reported Table 2.

1.5. Density measurements

Bulk densities of the materials were determined from geometric method. Indeed, the material, porous, cannot be in contact with liquid.

In equation (1) and (2), D represents the density, M the mass and V the volume.

$$D_{bulk} = \frac{M_{tot}}{V_{tot}} \quad (1)$$

Where $V_{total} = V_{material} + V_{\text{opened pores}} + V_{\text{closed pores}} \quad (2)$

1.6. SEM observations

The microstructure (porosity, particles and grains organization) and the observation of the interface between the glaze and the material were examined using a HITACHI model SU-70 scanning electron microscopy (SEM) with EDS attachment. The green ware and the unfired glaze are porous materials and require a special treatment to be observed in the SEM. The samples have been dive in methyl methacrylate by means of the apparatus STRUERS labo Press-3 with an applied force of 25 kN at a temperature of 180 °C for 5 min. Then to obtain a flat surface, the samples were polished without water and carbon-coated. It is important to precise that the polishing step can modify and rearrange the porosity. That is why another sample preparation was used. Millimetric quadratic pieces of green and biscuit were directly applied on a sample rack.

Two other samples, BC_BL and C_BL (Table 2) were prepared for SEM. BC_BL and C_BL correspond to samples processed by slip casting; BC_BL was fired twice at 1000 °C and 1350 °C whereas C_BL was fired only once at 1380 °C. These last samples, although less porous and coherent material, were poured into the resin as well, and polished for several hours by means of sand papers and diamond paste in order to get the surface as flat as possible.

Table 2. Green, biscuit, BC_BL and C_BL. identification and firing treatments of slip-casted samples.

sample	*green*	*biscuit firing*	*glost firing*	*slip casting*
		1000°C	*1380°C*	
green	x			x
biscuit	x	x		x
BC_BL	x	x	x	x
C_BL	x		x	x
stoneware	x			x

1.7. Weight measurements

The first stage of the work consisted in selecting some green pieces in the production line from the 3 different processes: slip casting, plastic molding and powder pressing. The weight of the pieces after each step of the process was measured as described Figure 7. These measurements were done in order to estimate the glaze and the water absorption and the water loss by the green and the biscuit.

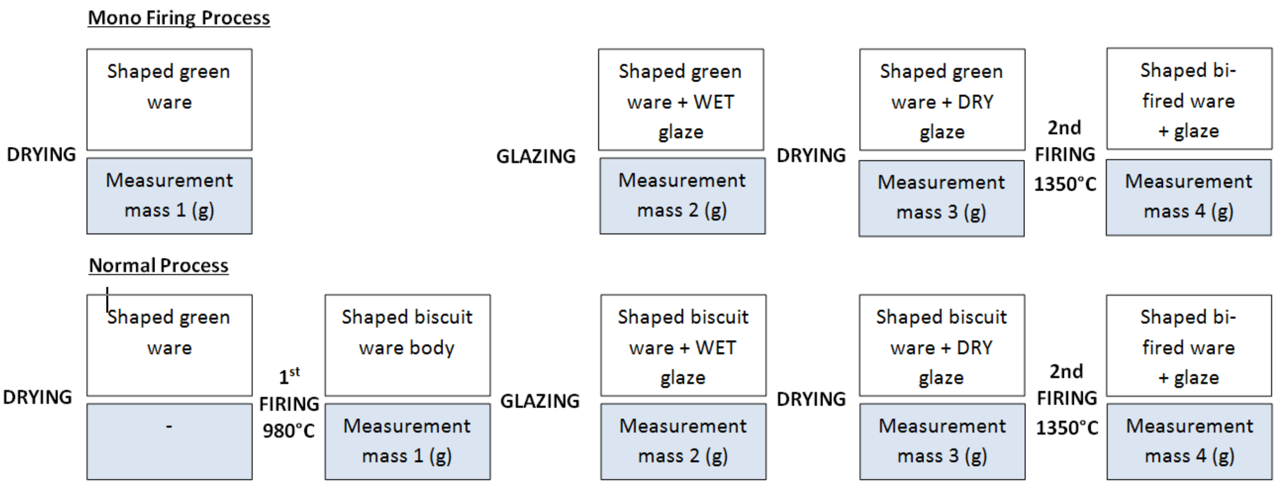


Figure 7. Operating procedure for the weight measurement after each step

1.8. Brunauer–Emmett–Teller (BET) analysis

The Specific Surface Area (SSA) is calculated according to the BET equation (3) and withNitrogen (N_2) gas:

$$\frac{p}{V(p0-p)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} * \frac{p}{p0} \quad (3)$$

Where V is the volume of N_2 adsorbed, Vm the monolayer volume of N molecule, p the sample pressure, po the saturation pressure and c the BET constant. From the equation (3) we can calculate the SSA from Vm :

$$SSA = \frac{V_m * n_a * a_m}{m * V_L} \quad (4)$$

Where n_a is the Avogadro constant, a_m the section area occupied by one N_2 molecule, m the weight of the sample and V_L the molar volume of nitrogen gas at the standart temperature and pressure (STP) (22414 cm3).

Nitrogen adsorption is a relevant method for the characterization of porosity. According to the International Union of Pure and Applied Chemistry (IUPAC) chart, microporosity determined with N_2 corresponds to pores with a size below 2 nm. Mesopores have a size in between 2 and 50 nm and macrospores have a size in between 50 and 100 nm (approximately). The characterization of the big pores is not accurate with this method. A method widely used to characterize pores with a size from 3 nm to 200 µm is mercury porosimetry (although it is not a friendly environmental experiment). This experiment has not been realized in this study but the combination of mercury and nitrogen adsorption could allow a more complete characterization of the pore distributions. Samples before adsorption were heated at 200 °C in order to remove the water molecules.

Another method called t-plot was also used. This method was proposed by Lippens and Boer (Lippens, et al., 1964) and it was used in this study in order to detect the presence of micropores.

1.9. Dilatometry Analysis

Dilatometer analysis were performed in order to check if all the reactions occurring in the sample bi-fired at 1000 °C and 1380 °C took place in the sample simply fired at 1380 °C. Dilatometer analyses were realized from the apparatus BärH GmbH 2000 equipped with a thermocouple type B. This analysis consists in recording the thermal change of length of a body as a function of the temperature. Heating rate used is 25 °C/min until a maximum temperature of 1400 °C.

2. Results

2.1. Determination of the problematic steps

As stated before, one of the major objectives of this work is to map the main problems that appear when, using the fabrication process of Costa Verde, the first firing is eliminated (biscuit firing), for the different processing methods (slip casting, plastic moulding (Roller, jiggering and jigging) and powder pressing). For that mono-firing trials were conducted directly on the production line for several pieces and the different processes. With this approach the major problems were revealed and are summarized in the three following diagrams.

The defects were mainly observed during the glazing step, the finishing step and after the gloss firing as well. It is important to note that in the bi-firing process, these two steps (glazing and finishing) take place after the biscuit firing.

2.1.1. Defects observed during glazing step

The glazing step, manual or automatic, consists in diving the piece into a glaze solution and requires an accurate gesture from the glazer. In the following parts, the description of all the problems encountered during the glazing step of the pieces of each process, will be described.

a- Slip casting process

The number of defects observed during the glazing of the pieces processed by slip casting was the most important. The biggest models of pieces presented the most problematic defects such as long or triple cracks appeared few second after the glazing step (Figure 8 B). On Figure 8-A it is observed that the piece totally broke at the contact point hand of the glazer/piece. These types of defects are irreversible.

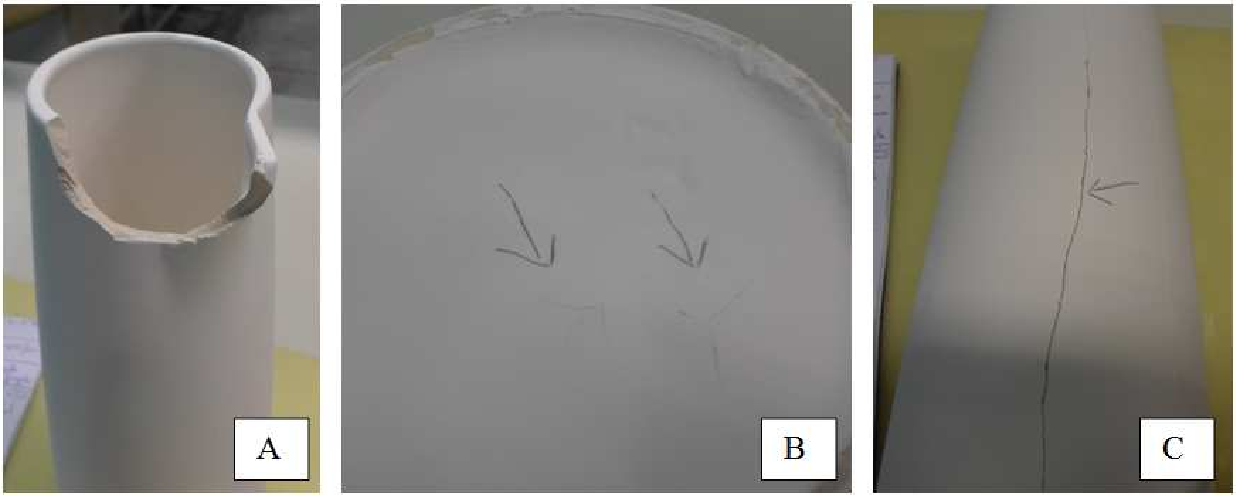


Figure 8. Defects observed during the glazing step for slip casting pieces

The defects observed for the small pieces processed by slip casting were not as important as the defects observed for the big ones. Most of the time these defects consisted in lake of glaze (Figure 9) at the bottom of the small tableware but no crack was noticed.

Figure 9. Lake of glaze due to a bad absorption observed at the surface of slip casting pieces

b- Roller jiggering process

The number of wasted pieces due to irreversible defects was very low in the case of the objects processed by roller jiggering. The crack observed Figure 10 was an isolated case. The small defects observed were mainly due to the contact with the hand of the glazer on the piece which causes a lake of glaze in a localized area or a small mark.

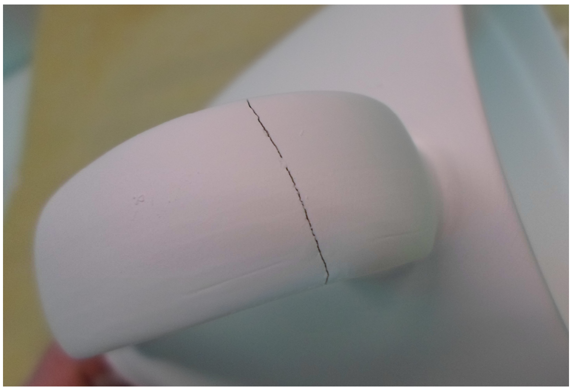


Figure 10. Irreversible defects observed during the glazing of the piece processed by roller jiggering

c- Pressing process

The manually glazed object processed by pressing, did not present so many problems. Generally some lacks of glaze were noticed in the edge and marks due to the contact with the hand of the glazer were observed.

2.1.2. Defects observed during the finishing step

The finishing step follows the glazing and consists in removing the excess of glaze from the bottom of the pieces. The pieces are manually or automatically clean with a sponge rubber deglazing belt saturated with water (Figure 11).

Figure 11. Finishing step with a sponge rubber deglazing belt saturated with water

The problems encountered during the manual step are the same for the pieces of the different processes. Usually, the glaze and the paste are removed with the belt. If the removing of the glaze at the bottom is wanted, the removing of the paste on the contrary is unwanted. Indeed, it modifies the initial shape of the object (Figure 12).

Figure 12. Paste removal during the manual finishing step (slip casting process)

2.1.3. Automatic finishing and glazing steps

Usually, plates or dishes processed by roller jiggering and pressing, are glazed and finished automatically. The apparatus used, works with aspiration cups (Figure 13) to move the plates from one place to another. In this process, plates undergo two forces; the pressure due to the aspiration and the gravity linked to their own weight.

Figure 13. Aspiration cup for dishes used for automatic glazing and finishing.

The defects observed are important and the same for the two processed. As represented on Figure 14 it is clearly observed that the high pressure applied by the aspiration cup break the center of the dishes. If this does not happen at the beginning of the automatic process it happens very often after the glazing or the finishing step.

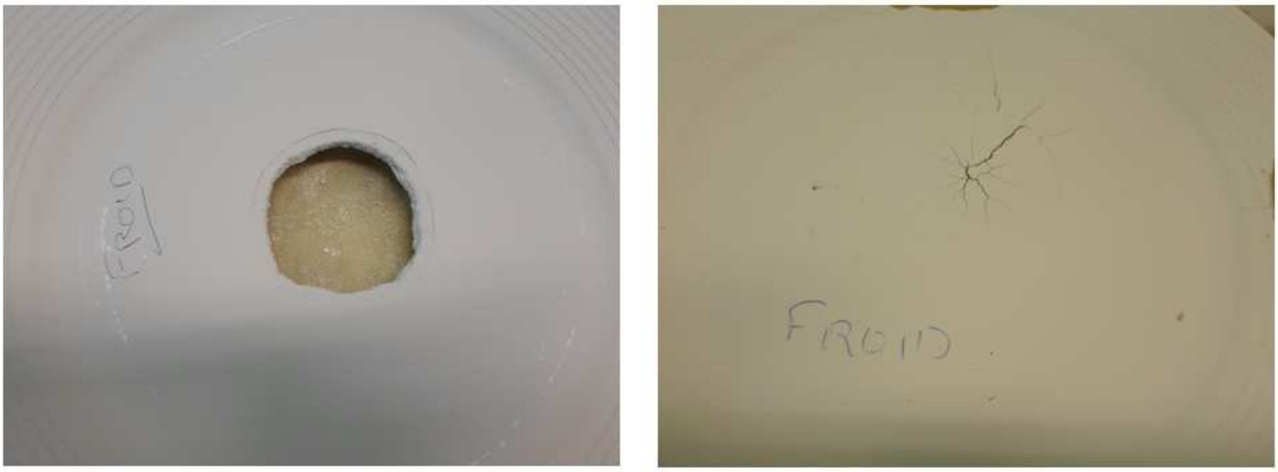


Figure 14. Defects observed before the glazing and the finishing step (pressing)

If, by chance the pieces succeed to reach the finishing step without being broken by the aspiration cup, many defects appear during the finishing step (Figure 15). Projection of small balls of pastes can be observed at the bottom of the dishes, cracks in the middle of the plates due to the pressure of the aspiration cup appear very often and excess of paste removal can also be observed.

Figure 15. Defects observed after the automatic finishing step (pressing and roller jiggering processed)

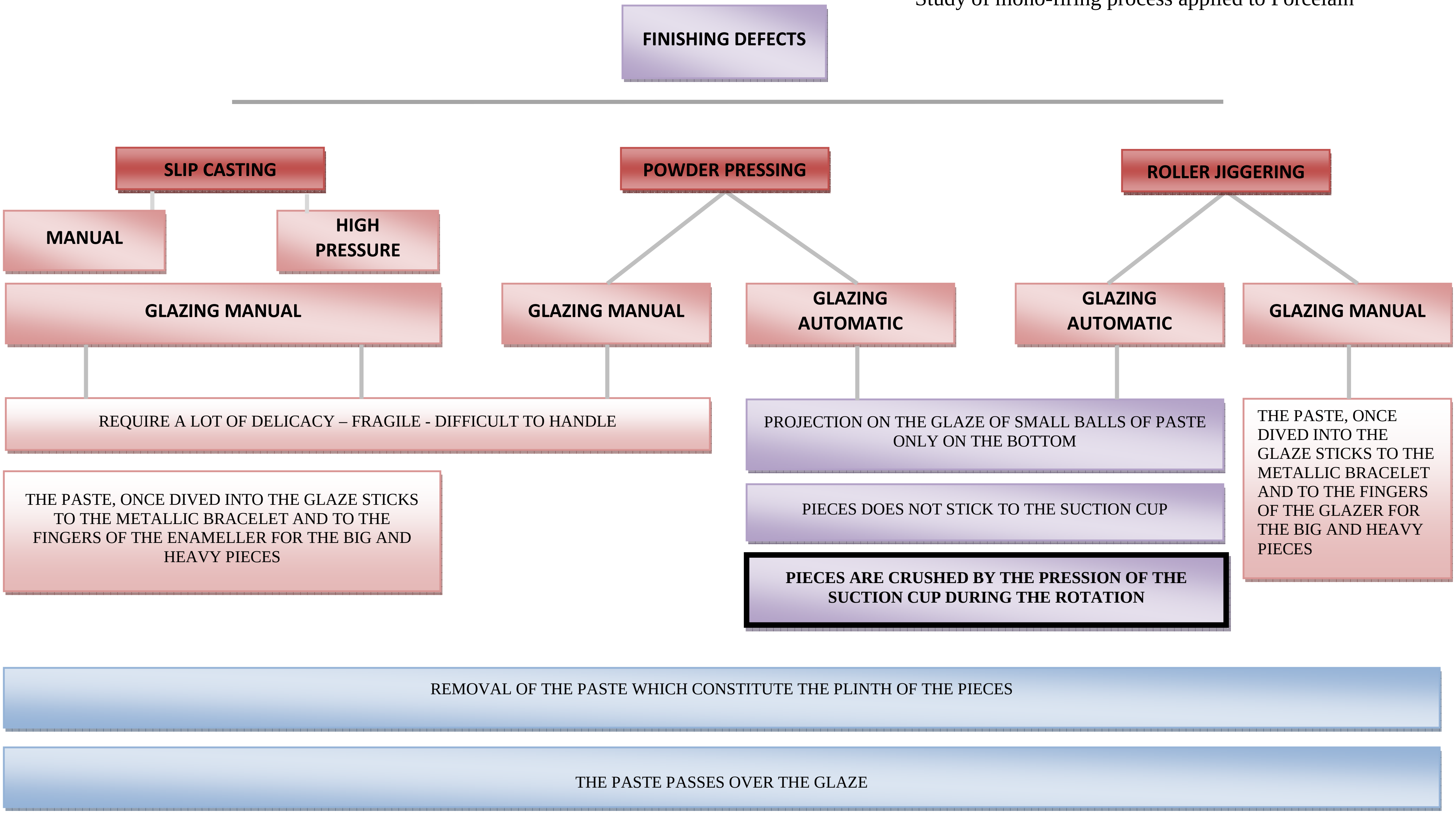
Finally, in order to better visualize all the defects, three diagrams has been realized.

2.1.4. Listing of defects observed

GLAZING DEFECTS

- **SLIP CASTING**
  - **MANUAL** / **HIGH PRESSURE**
    - **GLAZING MANUAL**
      - LACK OF GLAZE ON THE EDGE
        - APPEARANCE OF TRIPLE CRACKS AT THE BOTTOM
        - **APPEARANCE OF LONG CRACKS**
        - **BIG PIECES: BREAK EASILY AT THE CONTACT POINT HAND/PIECE**
        - **SWELLING AND BREAKING OF THE PASTE**
        - APPEARANCE OF SMALL LUMPS AND BUBBLES
      - LACK OF GLAZE
        - THE PASTE, ONCE DIVED INTO THE GLAZE STICKS TO THE METALLIC BRACELET AND TO THE FINGERS OF THE GLAZER FOR THE BIG AND HEAVY PIECES
        - CAN NOT BE PUT DOWN EASILY
        - REQUIRE A LOT OF DELICACY TO HANDLE
        - APPEARANCE OF MANY BUMPS WITH A CRACK IN THE MIDDLE
- **POWDER PRESSING**
  - **GLAZING MANUAL**
    - LACK OF GLAZE ON THE EDGE
    - THE PASTE, ONCE DIVED INTO THE GLAZE STICKS TO THE METALLIC BRACELET AND TO THE FINGER S OF THE GLAZER FOR THE BIG AND HEAVY PIECES = CAUSES INDELEBILE MARKS ON THE PIECES
    - REQUIRE A LOT OF DELICACY TO HANDLE
  - **GLAZING AUTOMATIC**
    - THE PIECES COLLAPSE UNDER THEIR OWN WEIGHT WHEN THEY ARE TRAPPED BY THE SUCTION CUP
    - AFTER THE GLAZING, THE PIECES DOES NOT STICK TO THE SUCTION CUP
    - <u>LUMP</u> + <u>CRACKS</u> WHICH CONVERGE TOWARDS THE MIDDLE OF THE PLATE = DUE TO THE SUCTION
    - CIRCULAR CRACKS
    - APPARITION OF CRACKS: CONTACT POINT BETWEEN THE SECTION CUP AND THE GREEN BODY.
- **ROLLER JIGGERING**
  - **GLAZING AUTOMATIC**
    - THE PIECES COLLAPSE UNDER THEIR OWN WEIGHT WHEN THEY ARE TRAPPED BY THE SUCTION CUP
  - **GLAZING MANUAL**
    - LACK OF GLAZE
    - THE PASTE, ONCE DIVED INTO THE GLAZE STICKS TO THE METALLIC BRACELET AND TO THE FINGER S OF THE GLAZER FOR THE BIG AND HEAVY PIECES

GLAZING STEP EASIER FOR THE ENAMELLER WHEN THE PIECES ARE WARM =PIECES <u>**SEEM**</u> **MORE RESISTANT**


FINISHING DEFECTS
SLIP CASTING
POWDER PRESSING
ROLLER JIGGERING
MANUAL
HIGH PRESSURE
GLAZING MANUAL
GLAZING MANUAL
GLAZING AUTOMATIC
GLAZING AUTOMATIC
GLAZING MANUAL
REQUIRE A LOT OF DELICACY – FRAGILE - DIFFICULT TO HANDLE
THE PASTE, ONCE DIVED INTO THE GLAZE STICKS TO THE METALLIC BRACELET AND TO THE FINGERS OF THE ENAMELLER FOR THE BIG AND HEAVY PIECES
PROJECTION ON THE GLAZE OF SMALL BALLS OF PASTE ONLY ON THE BOTTOM
PIECES DOES NOT STICK TO THE SUCTION CUP
PIECES ARE CRUSHED BY THE PRESSION OF THE SUCTION CUP DURING THE ROTATION
THE PASTE, ONCE DIVED INTO THE GLAZE STICKS TO THE METALLIC BRACELET AND TO THE FINGERS OF THE GLAZER FOR THE BIG AND HEAVY PIECES
REMOVAL OF THE PASTE WHICH CONSTITUTE THE PLINTH OF THE PIECES
THE PASTE PASSES OVER THE GLAZE

GLOST FIRING DEFECTS

SLIP CASTING

MANUAL

HIGH PRESSURE

GLAZING MANUAL

- SOME CRACKS APPEAR ONLY AFTER FIRING
- MARKS OF SHOCK
- LACK OF GLAZE
- IN SOME CASE IMPORTANTE DEFORMATIONS
- AS FOR THE BI-FIRED PRODUCTS, HANDLES NEED TO BE RE-GLAZED
- PRESENCE OF EXPLOSED BUBBLES

- MARKS OF SHOCK
- LACK OF GLAZE
- PRESENCE OF LUMPS
- NO DEFORMATION OBSERVED

POWDER PRESSING

GLAZING MANUAL

- IN RARE CASES SOME IMPORTANTE DEFORMATIONS
- SLIGHT DEFORMATIONS

GLAZING AUTOMATIC

- SOME CRACKS APPEAR AND ARE VISIBLE ONLY AFTER FIRING
- AS FOR THE BI-FIRED PRODUCTS, HANDLES NEED TO BE RE-GLAZED

ROLLER JIGGERING

GLAZING AUTOMATIC

- SLIGHT DEFORMATIONS

GLAZING MANUAL

- AS FOR THE BI-FIRED PRODUCTS, HANDLES NEED TO BE RE-GLAZED

APPEARANCE OF SMALL BLACK STAINS (paste contamination)

ROUGH TO THE TOUCH AT THE BOTTOM OF THE PLATES

SURFACE RIDDLED WITH SMALL HOLES

NO DEFORMATION FOR THE CUP OR THE SMALL PIECES IN GENERAL

CHANGE IN COLOR

The previous diagrams show also clearly that the mono-firing process does not cause the same type of defects and the same number of defects for all the processing, there is a direct dependence on the type of defect and their incidence on the used shaping process. Pieces processed by slip casting and pressing are much more affected by mono-firing process than the ones processed by roller jiggering. For the case of slip casted pieces the major problems are the appearance of long cracks observed just after the glazing step. For the case of pressing the major problems are the small dots spread on the final product.
However the lake of glaze appears several times and for all the process. It is due to a bad glaze adhesion at the surface of the green.

2.1.5. Weight difference observed between the biscuit and the green

According to the glazer, the glazing step was harder in part because of the important weight of the pieces. The weight of the biscuit and the green has been compared (Table 3). The weight of the green is higher than the weight of the biscuit.

Table 3.Mass difference between green and biscuit (slip casting)

	slip casting		
	piece 1	piece 2	piece 3
mass green (g)	128.42	702.3	162.9
mass biscuit (g)	117.1	607.4	134.7
LOI (% wt)	8.8	13.5	17.4

This difference is due to two main reactions. The first takes place around 100 - 200 °C and corresponds to the loss of weakly bond water to the clay particles. The second reaction is caused by the reaction of dehydroxylation of the kaolinite which occurs between 500 – 600°C. Pure kaolin minerals can lose up to 14 wt. % when heated at this temperature range (Christidis, 2011). To conclude, this important difference of weight observed between the green and the biscuit corresponds to the Loss on Ignition (LOI). The heavy weight of the green body partly due to the remaining of the structural water will have a direct impact on the handling of the piece by the glazer.

2.1.6. Glazer work

The work of the glazer refers to the facility to glaze. Easier the glazing higher will be the number of successful pieces. According to the glazer (the person in charge of the applying the glaze on the pieces), warm pieces are easier to enamel than the cold ones. This can be due to the fact that in contact of the warm piece, the water contained in the suspension of glaze evaporates. The observation of a thin vapor around the piece when they are removed from the solution is an argument in favor of this hypothesis

2.1.7. Comparison Weight % Glaze between the green and the biscuit

Once glazed, the piece, the amount of glaze bond at the surface of the piece was calculated simply thanks to difference of mass. The mass of the green (or biscuit) was subtracted to the mass of the piece with the glaze (dry).

Figure 16, Figure 17 and Figure 18 represent the weight percentage (wt %) of glaze absorbs at the pieces surface versus the weight (g) of the pieces. Each color corresponds to one model of piece. The experiment was realized for each process. The triangular points represent the amount of glaze absorbed at the surface of the biscuit whereas the circular points represent the amount of glaze absorbed at the surface of the green. A general trend appears clearly: the triangular points (representing the biscuit) have, for every pieces of each process, higher values than the circular points (amount of glaze at the surface of the green). This means that the glaze bonds easier to the surface of the biscuit than to the surface of the green ware. This observation is valid for all the processes (slip casting, pressing and roller jiggering).

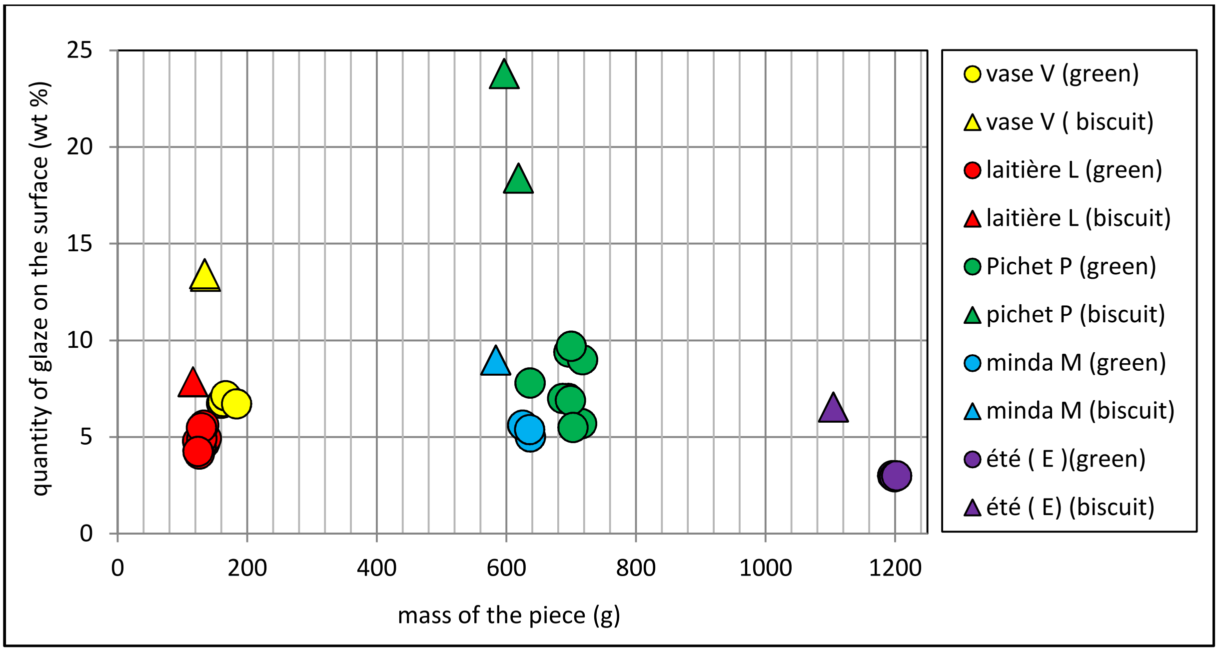


Figure 16. Absorption of the glaze (in weight %) with a density of 1380 kg/m^3 for liquid paste (slip casting)

The results obtained for Roller jiggering process (Figure 17) show the same trend, although the differences in glaze absorption are much less important than in the case of the slip casting.

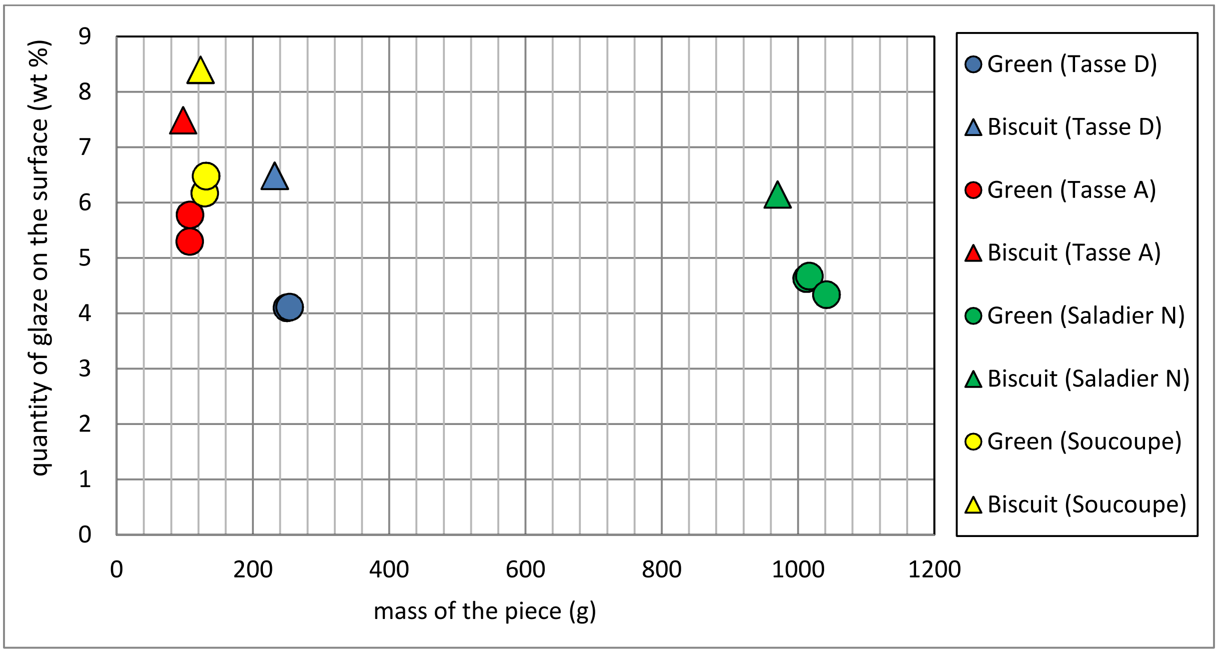


Figure 17. Absorption of the glaze (in weight %) with a density of 1380kg/m^3 for plastic paste (Roller)

In the case of powder pressing, the differences in glaze absorption are much more obvious than for the roller jiggering process.

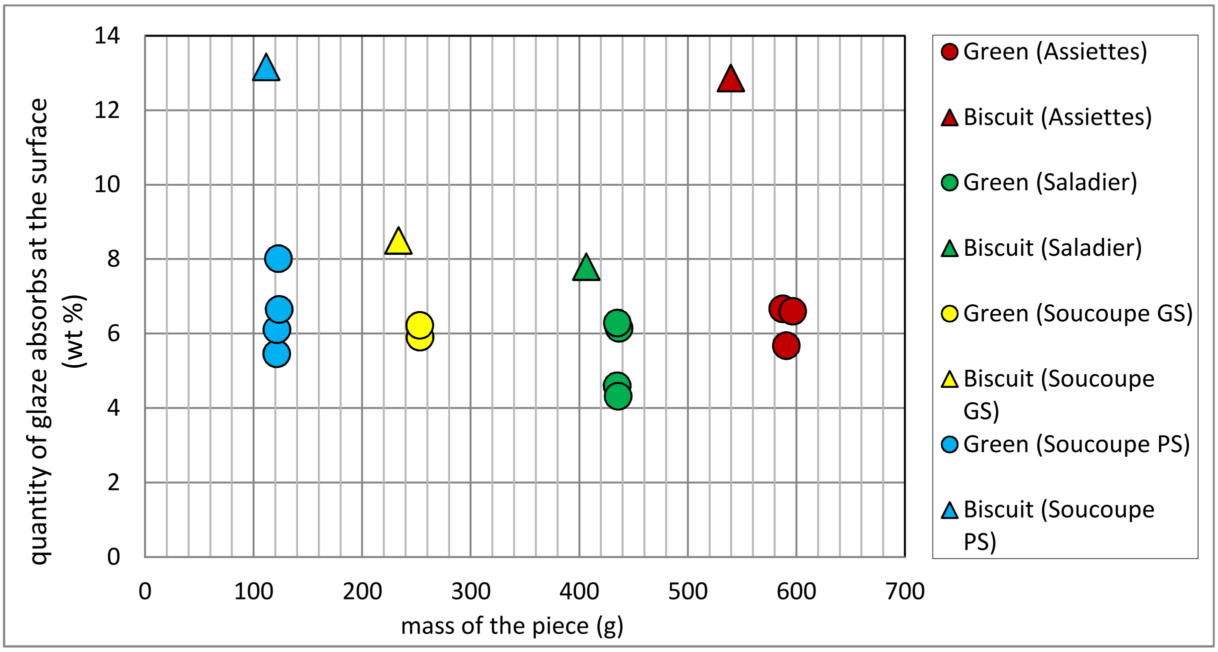


Figure 18. Absorption of the glaze (in weight %) with a density of 1380 kg/m^3 for pressing

Although the biscuit always absorbs more glaze than the green, the quantity of glaze is quite random and seems to depend on the model, process used to shape the piece, time spend immersed in the glaze, but not on the object mass. However, it clearly appears that the biggest differences in glaze absorption between the green and the biscuit are observed for the pressing and slip casting process. This is probably due to the densification and so the size of the pores of the pastes used in the different shaping process.

In the case of the slip casting process, these results were confirmed with optical microscopic observations (Figure 19). The glaze thickness observed at the surface of the biscuit is higher than the one observed at the surface of the green ware for a same density (1380 kg/m^3) in the case of porcelain. As a comparison, the stoneware (monofired) shows higher thickness of absorbed glaze. The density of the glaze used in stoneware is much higher ≈1650 kg/m^3 than in the porcelain industry.

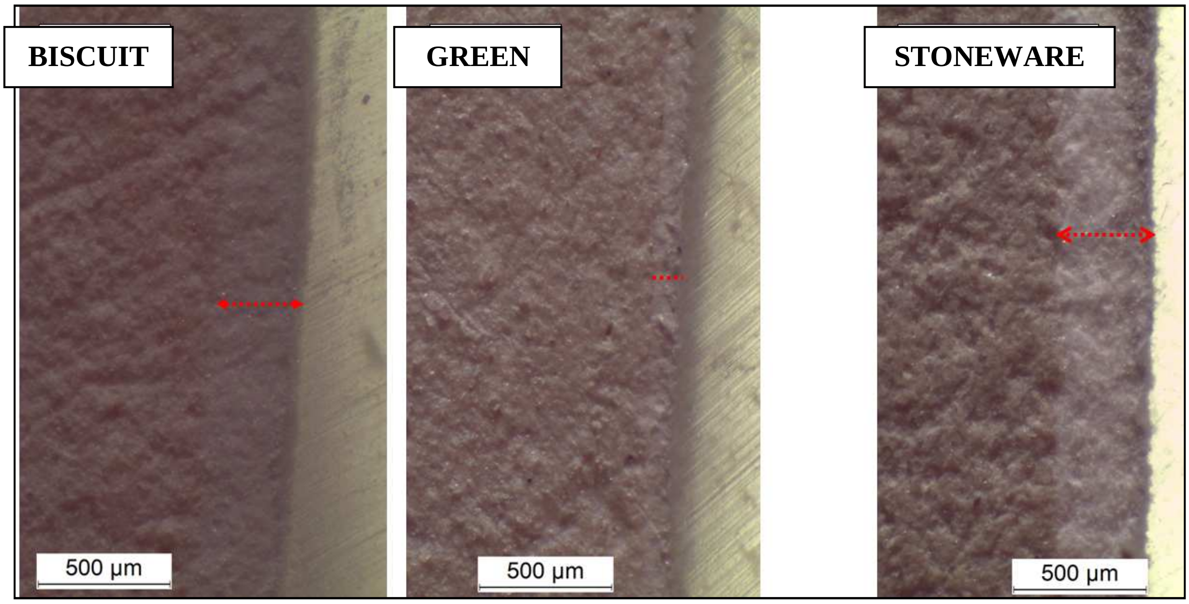


Figure 19. Optical micrographs of the interface between the ceramic body (biscuit, green porcelain and stoneware) and the glaze layer. The porcelain glaze density is1380 kg/m^3 while for stoneware glaze the density is 1650 kg/m^3.

2.1.8. Difference in water absorption during the glazing step between the green and the biscuit

As it is shown in Figure 7, the weight of the piece was measured just after the glazing step and then after the drying of the glaze applies on the pieces. The results can be found in Table 4, Table 5 and Table 6. These results will give an indication about the amount of water absorbed by the piece during the glazing.

Table 4. Water absorbed during the glaze (wt %); slip casting process

Piece	Water absorbed during the glazing	
	Green	Biscuit
Name	(wt%)	(wt%)
Vase V	8.2	15.5
Laitière L	6.4	11
Minda M	6.5	10.6
ÉTÉ E	5.8	9.8

Table 5. *Water absorbed during the glaze* (wt %); roller jiggering process

Piece	Water absorbed during the glazing	
	Green	Biscuit
Name	(wt%)	(wt%)
Tasse T	6	9.2
Tasse A	6.42	9.14
Tasse P	4.92	7.92
Saladier N	5.57	7.95

Table 6. Water absorbed during the glaze (wt %); pressing process

Piece	Water absorbed during the glazing	
	Green	Biscuit
Name	(wt%)	(wt%)
Petit saladier PS	6.7	9.8
soucoupe	6.56	9.6
assiette	6.17	13.47
Petite soucoupe	8	14.18

Previously it was observed that green pieces absorb lesser glaze than the biscuit. The result of water absorption during the glazing confirms this observation. The water absorbed during the glaze in weight % is higher for the biscuit than for the green ware. These results were expected, indeed higher the glaze absorption, higher the water absorption. Then it is normal to observe higher mass difference due to higher water absorption.

To conclude, the main differences observed between the green and the biscuit, concern the weight, the glaze and water absorption. The biscuit absorbs more water and glaze than the green. Then the shaping process seems having an impact on the glaze absorption. Also, the biggest difference in glaze absorption between the green and the biscuit where observed in the case of the slip casting process and the pressing. These are the processes which present the most important number of defects during the glazing.

2.1.9. Glazing with different glaze densities

Previously, it was observed that the glazing at 1380.5 kg/m^3 caused many defects such as the lake of glaze. In this part, a solution is proposed to avoid this lake of glaze. It was previously said that in the case of mono-fired stoneware, the used glaze density, was much higher than the glaze density used to glaze mono-fired porcelain. Therefore, to study the effect of the density of the glaze on the defects in the case of glazing green pieces for monofiring four higher glaze densities were used: 1650 kg/m^3 (which corresponds to the glaze density used for stoneware), 1550, 1500 and 1480 kg/m^3. Naturally, the flow rate of the glaze (expressed in ml/s) increases with the density. This phenomenon is unwanted. Therefore, to avoid the increase of the flow value, a small quantity of deflocculant was added to the glaze solution. To note that a high amount of deflocculating agent may cause the deposition of particles. This addition has to be realized carefully because a too important amount of deflocculating agent may cause the deposition of particles.
Table 7 gives the densities and the flow values for the glaze used to enamel the pieces of the different pieces.

Table 7. Glaze densities and glaze flow values

Glaze density *(kg/m^3)*	*Glaze Flow values* (ml/s^1)
1348 (normal density)	2.03
1650 (density used for stoneware)	1.04
1560	1.76
1550	2.58
1500	3.16
1470	2.94

Figure 20, Figure 21 and Figure 22 present the weight percentage of glaze absorbed by the green body versus the density of the glaze. These values of absorption by the green body are compared with the values of absorption of the biscuit for a normal density (1380.5 kg/m^3). Then, Table 8 gives the thickness of the glaze layer absorbed at the surface of the piece for the different values of glaze density.

The final objective of these experiments is to determine the best density range at which:

- the thickness of glaze absorbed by the green body is higher or equal to the thickness of glaze absorbed at the surface of the biscuit,

- the lowest weight percentage of glaze to be used in the case of mono-firing (to limit the consumption of glaze).

Figure 20, Figure 21 and Figure 22 show that the quantity of glaze absorbed at the surface of the green body varies with the glaze density. Higher the density, higher is the quantity of absorbed glaze at the surface of the piece until a certain limit (not indicated here).

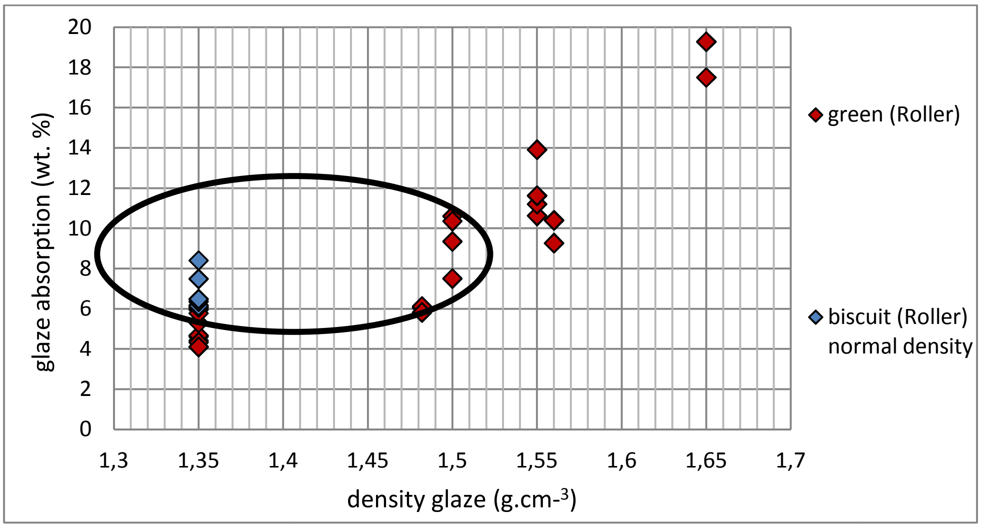


Figure 20. Absorption of the glaze (in weight %) with different densities for green ware and biscuit for roller jiggering process

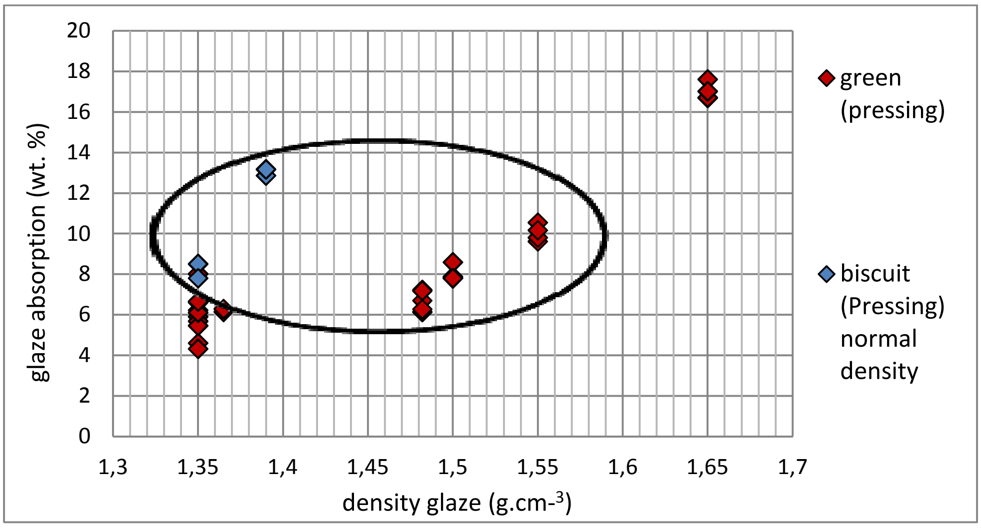


Figure 21. Absorption of the glaze (in weight %) with different densities for green ware and biscuit for pressing process

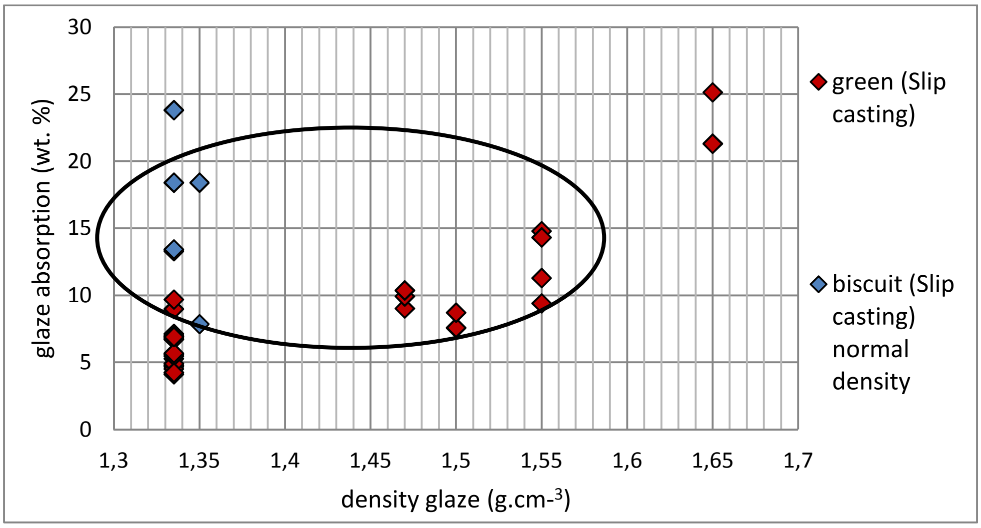


Figure 22. Absorption of the glaze (in weight %) with different densities for green ware and biscuit for slip casting process

Table 8. Density and thickness of the glaze layer absorbs at the surface of the pieces

Density	Thickness pressing	Thickness roller	Thickness slip casting
(kg/m^3)	*(mm)*	*(mm)*	*(mm)*
1650	0.55	0.6	-
1560	-	0.45	-
1550	0.35	0.45	-
1500	0.3	0.4	0.35
1482	0.3	0.35	0.3
1380,5 (biscuit normal)	0.25 - 0.3	0.3	

For roller process, a glaze with a density higher than 1500 kg/m^3 will present a percentage of weight absorption much higher than the one observed for the biscuit. This implies much higher glaze consumption. Moreover, the thickness of glaze absorbed at the surface of the green piece will be also much higher than the thickness of the glaze layer observed at the surface of the biscuit. Finally, the best compromise seems to work with a glaze density around 1480 - 1550 kg/m^3.

For pressing process, the density required seems to be in between 1480 - 1550 kg/m^3. Indeed, densities applied to the green body within this interval, show a similar thickness of the glaze absorbed at the surface of the piece and a percentage weight of absorption equal or lower than the quantity of glaze absorbed at the surface of the biscuit.

The best interval of densities required to glaze pieces from slip casting lies also in between 1480 and 1550 kg/m^3. Indeed, the weight percentage of absorbed glaze at the surface and the thickness of glaze measured, are similar to the ones observed for the biscuit.

However, in all of these cases these values of density need to be confirmed by the control of the aspect of the pieces after glost firing.

2.1.10. Observation of aesthetic aspect after glost firing for each process

The aspect of the piece was analyzed after the glost firing at a maximum temperature of 1380 °C for 6 h. Table 9, Table 10 and Table 11 sum up the defects observed.

Table 9. Observation aspect after glost firing at 1380 °C for 6h – Slip casting process

Density (kg/m^3)	*Piece*	*Defects observed after glost firing*
1650	large jug	glaze -run everywhere + piece very heavy
1550	large jug	glaze -run at the bottom of the piece + long and thin crack
1550	small milk jug	surface smooth (small lake of glaze on the handling)
1500	large jug	slight lake of glaze at the bottom of the jug
1500	small milk jug	surface smooth (small lake of glaze)
1482	large jug	No run-glaze but inside the jug lake of glaze but aspect much better

The aspect of the small pieces processed by slip casting does not present visible defects when glazed with different density glazes. Small pieces seem to be not affected by the glaze density change. Unlike small pieces, the big ones require a specific density. Indeed, above 1500 kg/m^3, the pieces, after glost firing present obvious run-glaze (Figure 23). Glazing the pieces with a density lower than 1380 kg/m^3 causes cracks, bumps ...which appear after or during the glazing step.

Figure 23.Defects observed after glost firing - use of different glaze densities: 1350 (density normally used in bi-fired process), 1482, 1500,1550 and 1650 (glaze densities use for glazing stoneware).

Table 10 .Observation aspect after glost firing at 1380 °C for 6h – Pressing

Density (kg/m³)	*Piece*	*Defects observed after glost firing*
1500	large plates	run-glaze in the middle of the plates + dots
1482	large plates	rough surface + dots
1500	saucer	surface smooth - small lake of glaze due to the finishing + dots
1482	saucer	smooth surface + dots

The aspect of the pieces processed by pressing presents many adverse hollows at the surface. These dots lower the quality of the pieces.

Table 11. Observation aspect after glost firing at 1380 °C for 6h - Roller jiggering

density (kg/m³)	*piece*	*defects observed after glost firing*
1550	saucer	smooth surface
1500	saucer	keep the details + feel the relief + few defects
1482	saucer	Good aesthetic aspect few defects

The aesthetic aspect of the pieces processed by roller jiggering is not impacted by the change of density. The general aspect of the pieces, from roller glazed with densities between the intervals 1480 - 1550 kg/m^3 is satisfactory.

However, these results concerned mainly the small pieces. For the large ones, despite the density change many defects are still present. But defects appearance is due to their important size which makes them difficult to handle.

2.2. Microstructure analysis

2.2.1. Mineralogical comparison between the green and the biscuit

XRD analysis were conducted to compare the mineral and phase compositions of the green and the biscuit bodies. The XRD patterns are presented in Figure 24. As expected the main difference between both samples, is the disappearance of the kaolinite after the first firing. The kaolinite didn't disappear totally, but turns into metakaolin, not observable on the XRD pattern. Indeed it is an amorphous aluminium-silicate with a disordered structure (Gastuche, et al., 1962). The mineral and phase compositions of porcelain fired twice (normal process) and fired only once at 1380 °C was also compared. Despite different number of firing, the mineral phases present in the samples are the same as expected. In both case the appearance of mullite occurs.

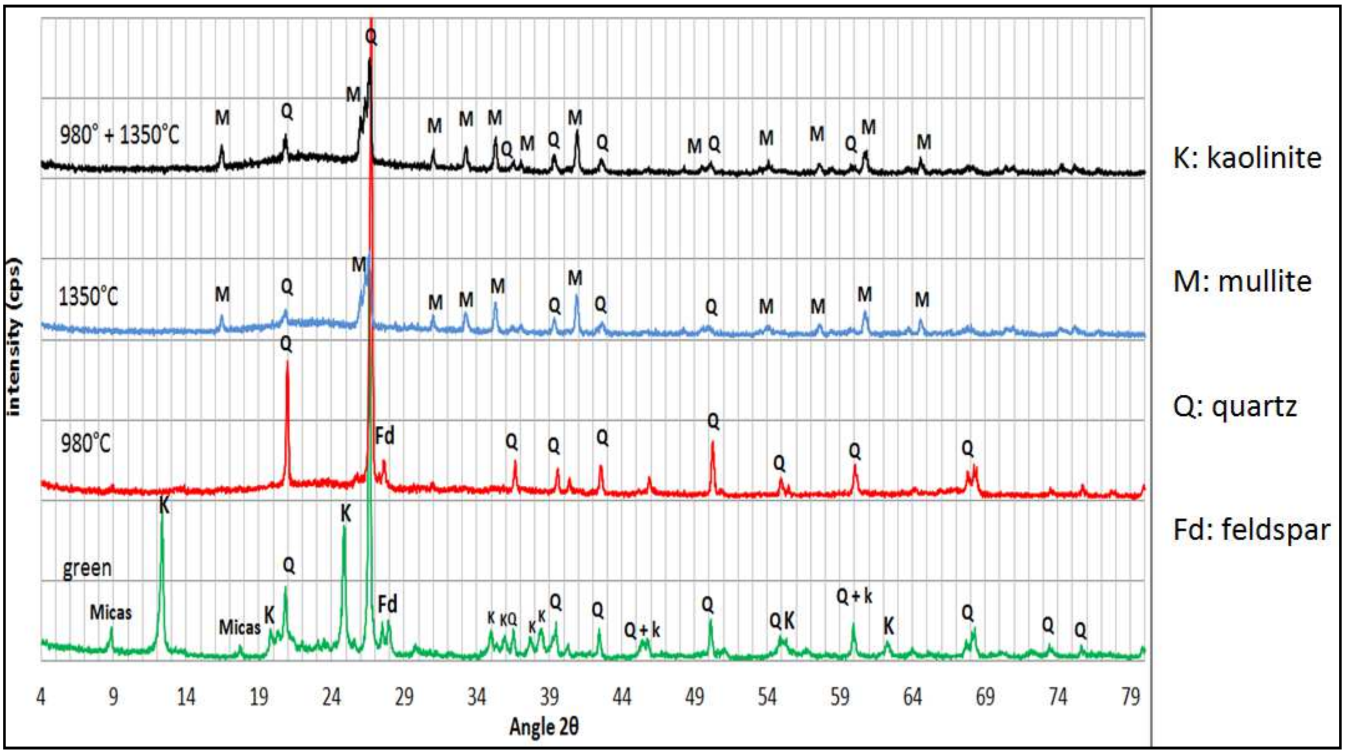


Figure 24. XRD patterns of the green body, biscuit, the final product of the mono-firing process, the final product of the bi-firing process -Mineralogical change as a function of the temperature of firing

The following SEM micrograph has been realized to visualize the organization of the pores at the surface of the pieces. The surface of the green body was compared by SEM with porcelain biscuit fired at 1000 °C; The green ware is covered by booklets of kaolinite which can reach 20 µm X (left). As expected after the first firing, the booklets of kaolinite disappeared after the first firing. The particles after firing are smaller and the edges are irregularly shaped. The biscuit seems to have a surface much more closed than the biscuit.

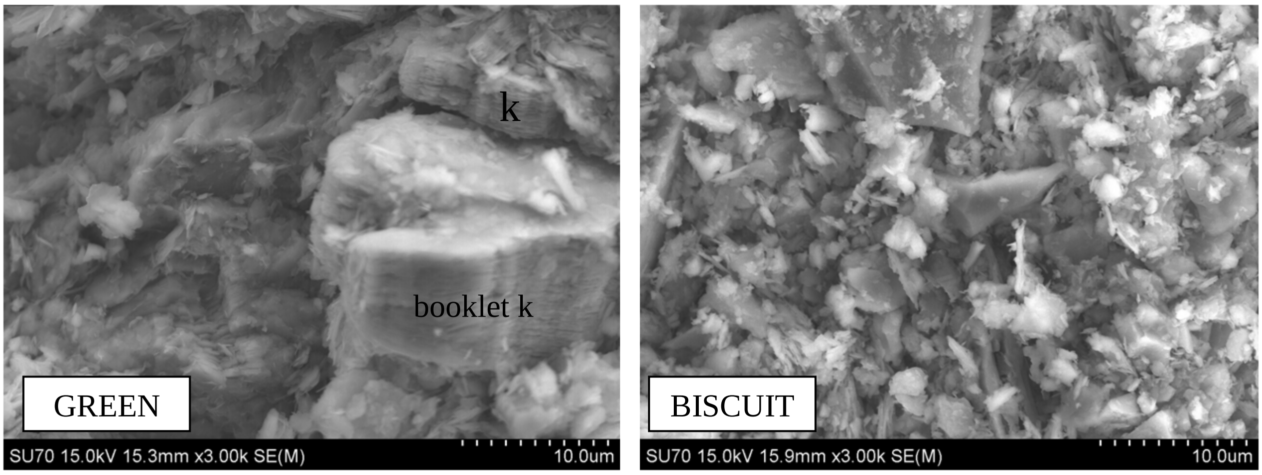


Figure 25. SEM micrograph of the surface (non polished) of the green ware and biscuit (slip casting) k: kaolinite

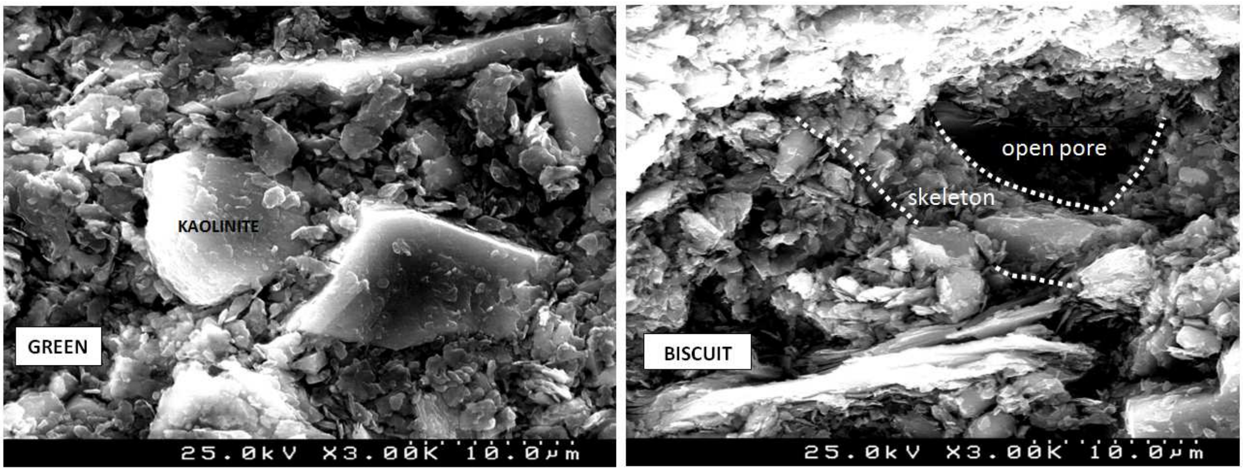


Figure 26. SEM micrographs of the surface of the green body (left) and the biscuit (right).

After the firing at 1000 °C, the biscuit shows in some localized areas a rearrangement of the particles. The latter seems forming packs. The number of big pores seems more important in the case of the biscuit than in the green (Figure 26).

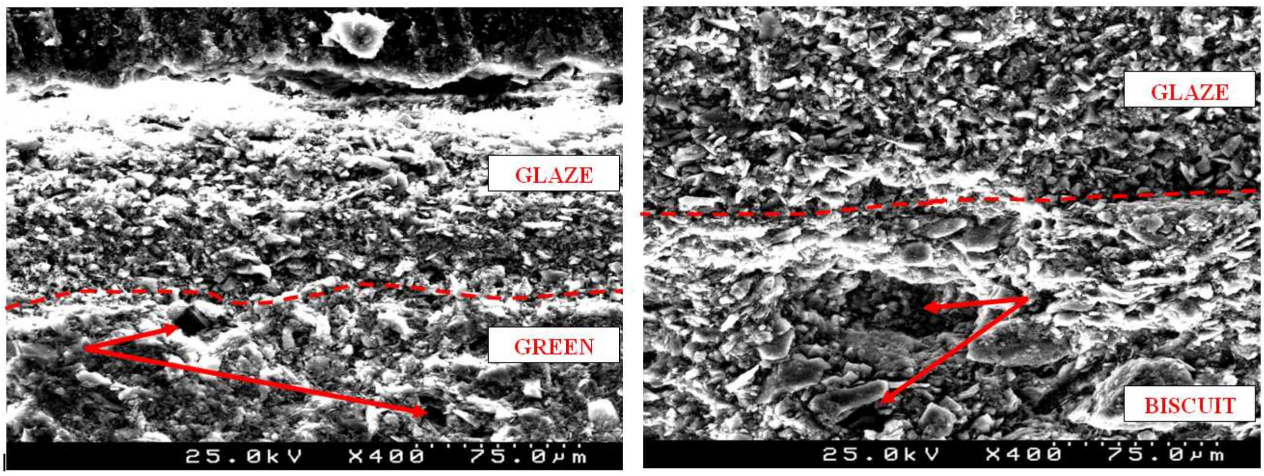


Figure 27. SEM micrograph - observation of the interface green/glaze and biscuit/glaze

Figure 27 does not show big differences between interface green/glaze and the biscuit/glaze. However the pores present in the biscuit are much bigger than in the green.

2.2.2. Nitrogen adsorption results

The objective of the N_2 adsorption analysis was to compare the SSA of the green and the biscuit. The SSA will Figure 28 represents the adsorption curves realized from the green and the biscuit sample of slip casting process. Both of the curves correspond to isotherm II. From these two isotherms and the t-plot method (Figure 29), external surface area, microporosity and specific surface area were determined.

Table 12. Specific surface area values for the green and the biscuit ware

SSA	
(m^2/g)	
Biscuit	Green
3.39	8.26
5.65	4.66
5.22	8.57

Table 12 shows that the SSA results are very low. According to the results, the green seems to have a bigger SSA than the biscuit. However it is hard to estimate how much bigger is the SSA of the green compare to the one of the biscuit. As the results are very low, the measurement error of the apparatus is non negligible. Therefore, the adsorption-desorption curves obtained for the green and the biscuit samples have to be exploited carefully. To be relevant, the experiment should be realized several times. Moreover, the main porosity of these two samples is an intergranular porosity between quartz and feldspars grains or between kaolinite layers. If the porosity between the kaolinite layers can be nanometric, the space between the bigger grains of quartz or feldspars can reach a diameter of several micrometers. These big pores cannot be characterized by the nitrogen adsorption. (Santos, et al., 2011) suggests that to be relevant, porosity has to be characterized with different techniques. Each method, based on different physical principles gives one type of information. . Realize different type of analysis could allow a complete characterization of the porosity.

However, the fact that the SSA for the green is higher than the biscuit, seems coherent. In the green body no reaction between the minerals occurred, and no densification due to grain boundarie appearance took place as well. The boundaries appearance, which begin in the biscuit, tend to decrease the porosity and this could explain the slight difference in SSA observed between the green and the biscuit. However, these surfaces contact between the particles in the biscuit are not easily observable after the first firing at 1000°C.

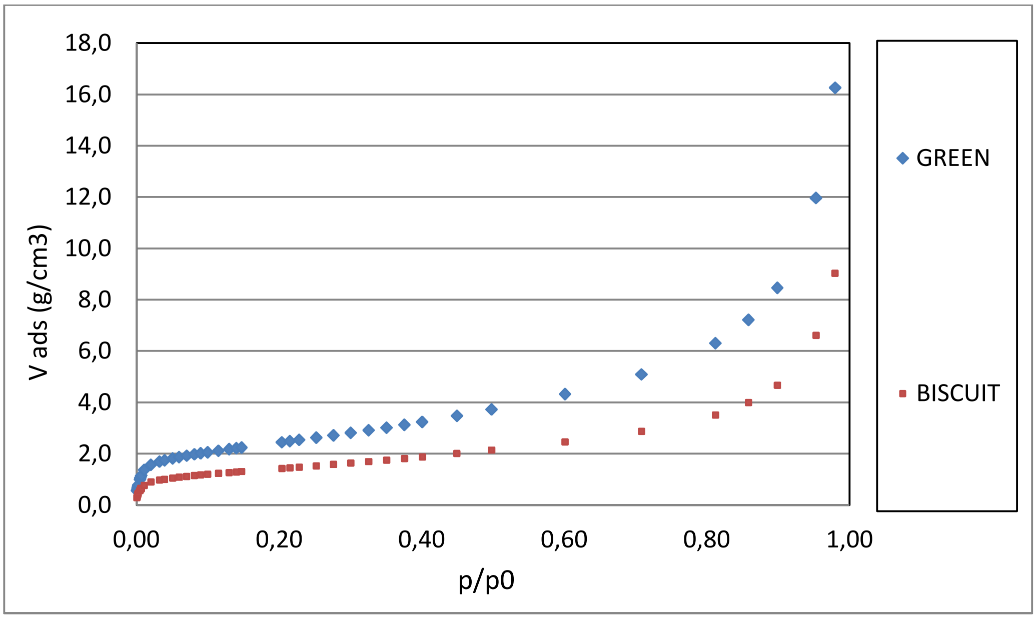


Figure 28. Adsorption curves for the green and the biscuit (slip casting): volume of adsorbed gas versus the gas partial pressure.

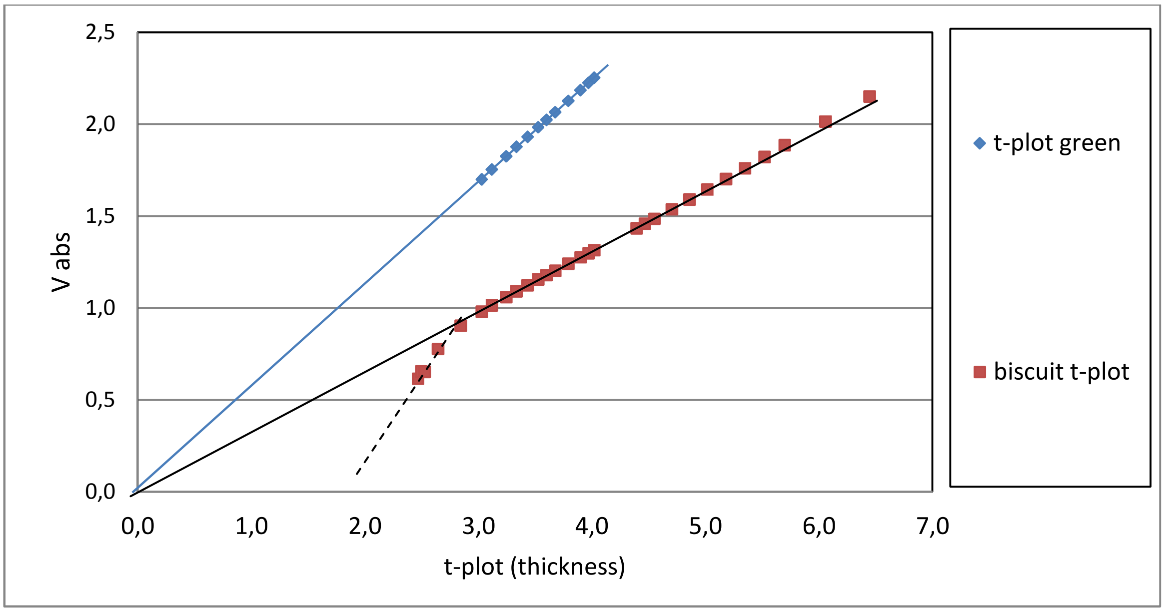


Figure 29. t-plot method to detect the microporosity of the green and the biscuit

According to Figure 29, t-curves cross the y axis at 0. This means no microporosity (Storck, et al., 1998). The slight difference in shape corresponds to different external surface area. The latter considers only open pores. The external area was estimated to be 8.6m² for the green and 5.22 m² for the biscuit.

These results are linked to the differences in porosity between the green and the biscuit ware. The bulk density for the green body shaped in slip casting process fluctuates in the 1.57 – 1.59 g/cm^3 interval while it varies in between 1.47 – 1.48 g/cm^3 for the biscuit.

Glost firing was done in a dilatometer and relative linear length change was detected Figure 30. The samples used for the dilatometry analysis were not glazed.

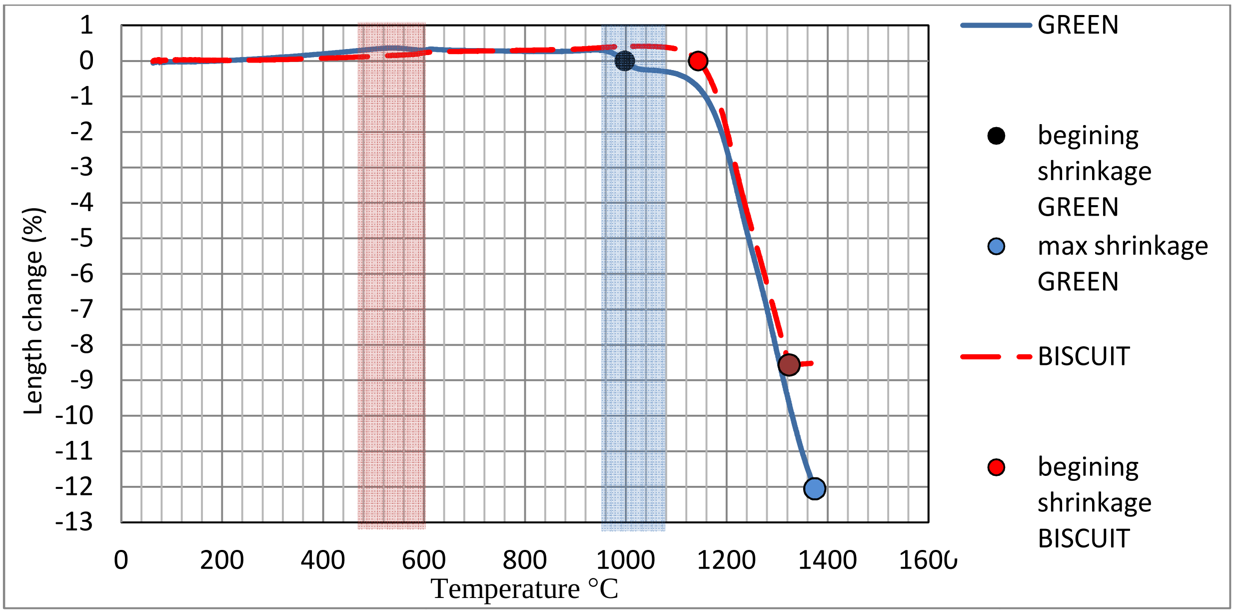


Figure 30. Shrinkage evolution for the biscuit and the green ware.

Figure 31, represents the derivative of the dilatometer results, and allow to better visualize the area with differences.

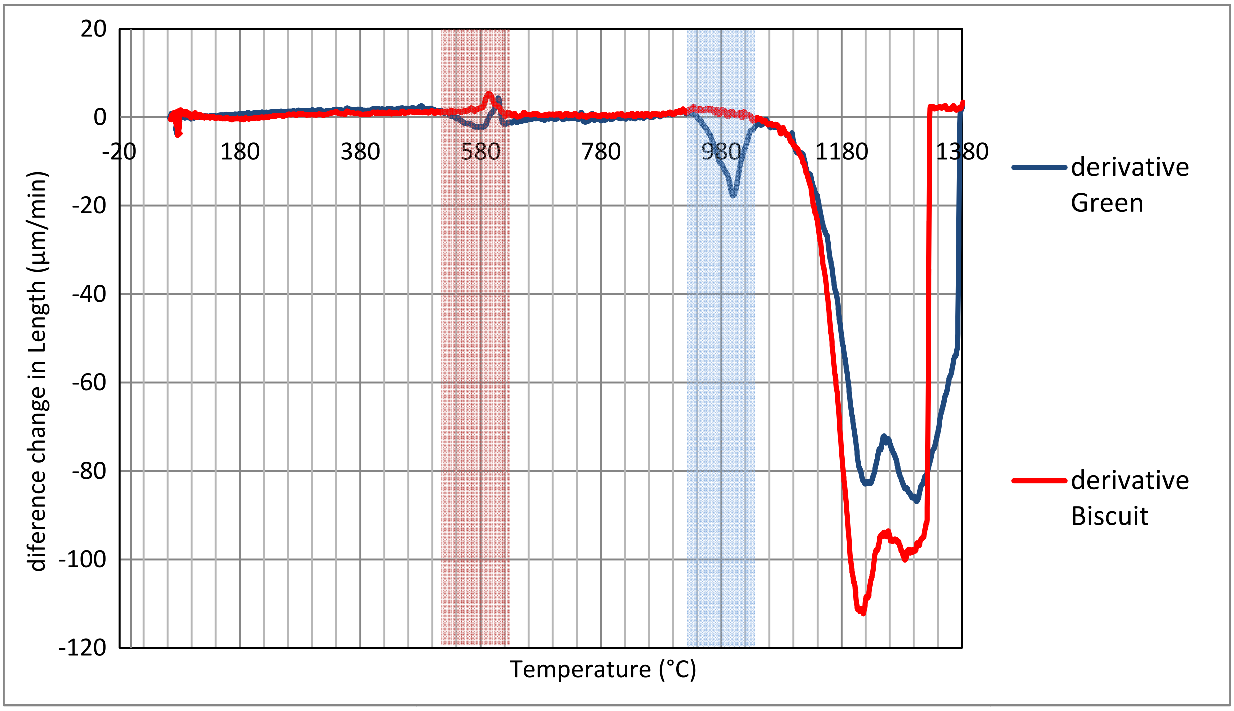


Figure 31. Derivative curve of the change in length versus temperature

The green body shows a first peak around 600 °C. This interval corresponds to the temperature at which kaolinite turns into metakolinite and quartz α turns into quartz β.

Then an important peak is observed only in the case of the green body around 1000 °C. This peak has two origins: the first one is the transformation of metakaolinite into primary mullite and the second one is related to the densification and the rearrangement of the porosity of the material. In the case of the biscuit, this reaction occurs in the first firing that is why this peak can not be observed on the dilatometry graph. Whereas in the case of the green this reaction will occur in the glost firing which takes place after the glazing and finishing step. These phenomenons (the transformation metakaolinite/primary mullite and the densification of the material) are two totally different reactions. However, one will help the other. The reaction metakaolinite/primary mullite is an exothermic reaction (Iqbal, et al., 2000). It means that it will give energy to the system. On the contrary, the densification requires energy to take place. At this step, around 1000 °C, the porosity decreased around 20%. To continue with the peak description, another peak is observed around 1230 °C. At this step the material get its higher density which means very low porosity.

Table 13. Results from dilatometry analysis

	Units	GREEN	BISCUIT
Beginning shrinkage temperature	(°C)	994	1142
End shrinkage temperature	(°C)	1378	1325
Relative linear length change	(%)	-12	-8,6

2.2.3. Comparison of the green and the biscuit densities

Green and biscuit densities were calculated from rectangular pieces. To avoid errors, the calculation has been done several times on several sticks. The density of the green was estimate at 1.48g.cm^{-3} whereas the biscuit density was estimated at 1.58 g.cm^{-3}. Conclusion the biscuit density is slightly higher than the density of the green. This observation can be link to the porosity. the biscuit should be a little bit less porous.

2.2.4. Comparison surface porosity after glost firing

SEM micrograph of the biscuit fired at 1380 °C (normal process) and the green monofired at 1380 °C do not present big differences in the porosity of the pieces. A bigger number of micrograph would allow a relevant comparison of the porosity distribution.

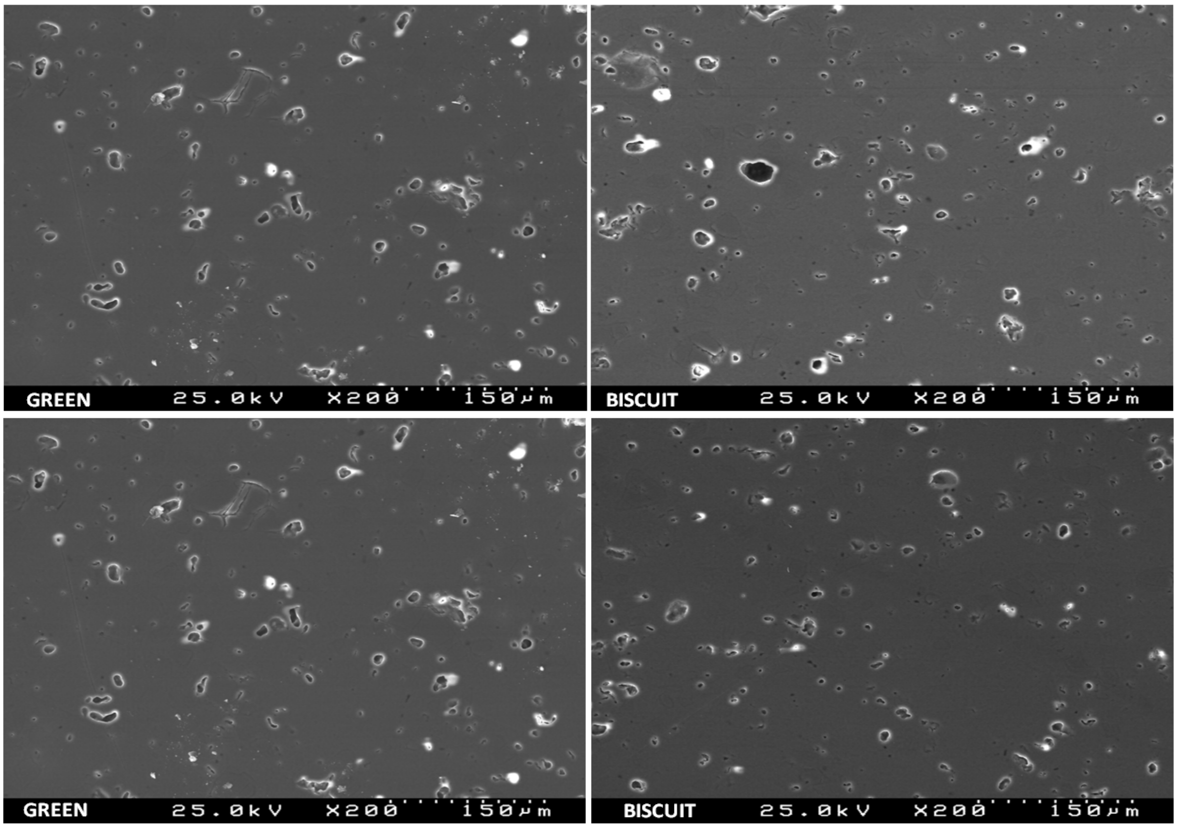


Figure 32. Comparison surface porosity of the green fired at 1380 °C and the biscuit fired at 1000 °C and 1380 °C

3. Discussion

The two problematic steps encountered during mono-firing are the glazing and the finishing step. This is to be expected because these two steps require manual or automatic handling, complicated by the high fragility of the green ware. In the normal bi-fired process, the enameled piece has been hardened by the first firing and densification defines a particular pore arrangement of the porosity and therefore can be handle without difficulty. However, it was not expected that the green body would absorb less glaze and water than the biscuit. This observation reveals another difficulty that needs to be got around to improve the results of mono-firing. But first of all the reason of this information requires to be explained.

3.1. Microscopic differences

The glazing experiment performed on the green and the biscuit body showed that the green body absorbed lesser glaze and less water than then biscuit.

First of all, the industries try to reduce the porosity of the green body at its maximum by compacting. The particles are well organized and the size of the pores are reduces as much as possible Figure 33.

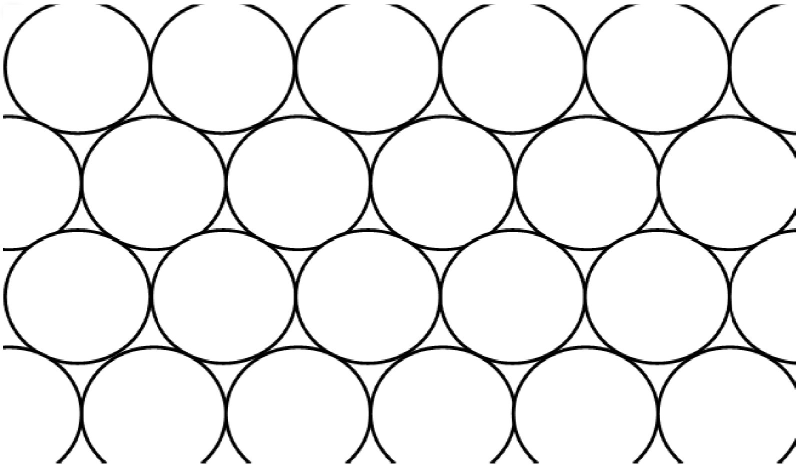


Figure 33. Representation of the green body with compact arrangement

The first firing realized at a maximum temperature of 1000 °C in the company of Costa Verde, will causes a rearrangement of the porosity. Grain boundaries will appear and the grains will be in contact as represented Figure 34. The surfaces contacts, appearing during the first sintering, are called “neck”. If the grain growth in one way, they have to decrease in another side. This displacement of the solid matter will create the apparition of “channel” in the material (Figure 34).

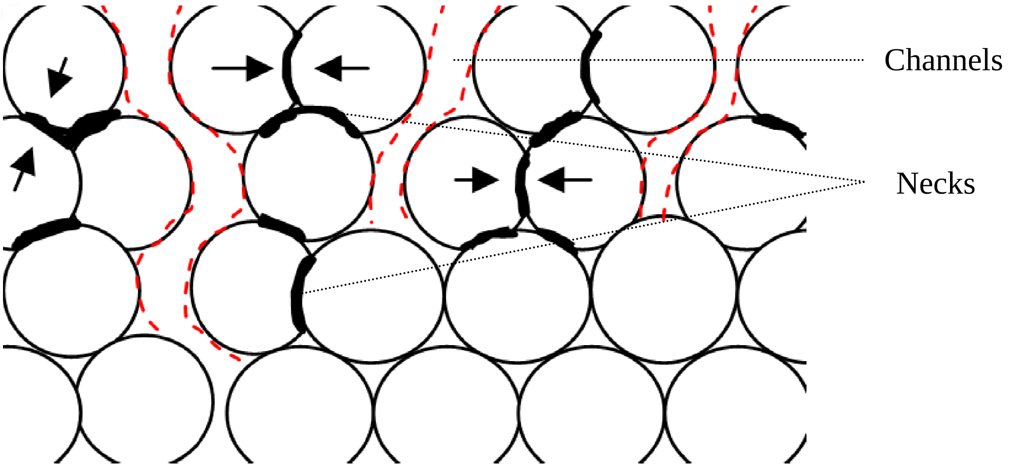


Figure 34. Representation of the biscuit fired at 1000 °C

The results of the dilatometry analysis strengthened this idea. Indeed, the peak presents at 1000 °C argues in favor of this densification. The measurements of densities emphasize the fact that the porosity is less important in the biscuit. Finally, the first firing allow to opened big pores and channels which then will allow a good adhesion of the glaze. The green body does not have such a porosity which preventing the penetration of the water and so the adhesion of glaze. The green body despite is important porosity remains impermeable to the water and glaze because of the small size of the pores. Unfortunately, the SEM micrograph did not allow to observe clearly this difference in arrangement of the porosity and the apparition of the surface contact between the grains.

As it is well described in the literature, (Bergaya, et al., 2006)… The main difference observed with the SEM micrograph is the presence of well crystallized kaolinite in the green, whereas in the biscuit, the kaolinite has been converted in metakaolinite. This reaction can have an impact on the rate of densification of the biscuit. Indeed it is an endothermic reaction, which means that it requires energy from the system. This can slow down the rearrangement of the porosity.

On the contrary, the reaction which leads to the formation of mullite from metakaolinite is a exothermic reaction which will provide energy to the system. This energy will help in the formation of the primary mullite. Then, this primary mullite helps at the densification of the material.

It is necessary now to propose solution to get around this problem. An easy way to deal with this problem consists in increasing the density of the glaze. The results showed that higher the density, higher was the glaze absorption at the surface of the green body. The difficulty is then to find the density of glaze required to form a layer on the green body as thick as the layer deposited on the biscuit, not to lower the aesthetic quality of the final product.

Despite these differences, mono-firing is far from being impossible to realize, but it requires some technical adaptations.

3.2. Adaptation for improvement of mono-firing process

3.2.1. Warming

According to the enameller, glazing when the pieces are warm allows a better glaze adhesion and avoids the accumulation of glaze in some localized areas. Indeed, a quantity of water in contact of the hot piece evaporates. This avoids the dislocation of the paste, localized at the contact point between the hands of the glazer and the piece. Therefore, before being glazed, the pieces could be stored in air dryer with high temperature. However, warming pieces requires energy therefore represents an additional cost.

3.2.2. Transportation

The green pieces are fragile and must be handled carefully. To avoid risks of shock, it is necessary to limit the number of displacements and handlings.

3.2.3. Glazing

The final products, from different processes and glazed with different densities were compared. Increasing the density makes the enameller work harder but it also improves the aesthetic aspect, until a certain limit. Moreover, the results obtained, differ depending on the process used upstream.
Therefore, the challenge is finding the right balance, between the work facility of the enameller, the final quality aspect and the quantity of the glaze which has to be as low as possible to reduce the final cost.

The results show that the mono-fired pieces realized by pressing, present all the same quality defect. Their surfaces are covered by many millimetric dots. Changing the density does not have any impact on the diminution of these dots. The density change will not impact much the final quality of the pieces processed by roller jiggering as well. It is not necessary to work with a very high value of density which increases the price of the porcelain production. Densities in the intervals of 1480 – 1550 kg/m^3 allow a good compromise between a satisfactory final aesthetic aspect, a low cost in glaze and a easy handling for the enameller.

Concerning the pieces processed by slip casting, choosing the right density is essential. The glazing realized on larges slip casting pieces shows that above a density of 1500 kg/m^3, the pieces present important defects such as run-glaze whereas with a density of 1380 kg/m^{3}causes defects such as cracks, bumps … Finally the best intervals of glaze density is restricted to 1480 kg/m^3 to 1500 kg/m^3 (for the large pieces).

The previous results showed that mono-firing process may be apply mainly to small and thick pieces such as saucer or small cups processed by roller jiggering. Indeed, their small size and light weight make them easier to handle. Moreover, their important thickness makes them harder to put out of shape during handling. The previous results show also that the glaze density in a quite important interval will not impact much the final aesthetic aspect.

The glazing of the biggest and fragile pieces could be done by automatic pulverization. This process would enable the manual handling. However it has to be test.

3.2.4 Finishing step

The finishing step remains a difficult part for the pieces processed by roller jiggering and slip casting. Indeed, cleaning the glaze from the plinth causes also the removal of the paste. The pieces processed by pressing are much less affected by this phenomenon. Currently, the only way to avoid the paste removal consists in avoiding an important pressure on the green piece.

3.2.5. Automatic glazing and finishing step

Automatic glazing and finishing steps show good results for roller jiggering process. However the pressure applied on the cup need to be adjusted beforehand.

The piece realized by pressing presented different results. Most of the plates really thin were broken by the aspiration cup. This is due to the too high pressure applied by the aspiration cup on the pieces.

To conclude the discussion, the improvements proposed above would improve the mono-firing process on porcelain. Although, it didn’t solve most of the problems encountered for the pieces process for pressing or slip casting. Additional studies need to be done in order to increase the quantity of pieces suitable for sale. It could be propose to focus the next studies on how to limit the manual handling. This could be realized through the use of equipments such as robotic spray glaze.

Conclusion

This study has shown the main problematic steps encountered when a bi-firing process is substituted by a mono-firing process to manufacture porcelain, namely the porcelain of COSTA VERDE SA.

The knowledge of the difficulties is necessary to then proposed adapted solutions. In this case, the problems encountered affect mainly the glazing and the finishing step. This is partly due to the low mechanical strength of the green body, which makes the handling of the pieces difficult but not only. Another reason related to the glazing step is linked to the porosity level and has been point out. It was observed that the green body, although more porous than the biscuit, does not facilitate the glaze and the water absorption because of the small size of the pores. On the contrary, the biscuit, exposed to a 1st sintering at a temperature of 1000 °C has developed into its structure some necks between the grains which increase the density. But simultaneously creates the formation of channel's of porosity between the particles that promote a good adsorption of the water and glaze. Although this particularity was observed for each process, the difference in weight percentage of glaze absorbed between the biscuit and the green body varies with the process and is higher for the slip casting and pressing process.

To overcome the lack of glaze at the surface of the piece, different glaze densities were used and it was observed that by adjusting the glaze density the glaze adhesion to the surface of the body improves. By selecting the correct glaze density similar results were obtained between bi-fired and mono-fired porcelain.

These preliminary results are very encouraging and open the way for other improvements that can be proposed as future work. First of all, the strengthening of the green body can be improved by the addition of binders. Alternatives to control the porosity of the green body can also become a good way to improve the glaze absorption.

Agrafiotis Christos and Tsoutsos Theocharis Energy saving technologies in the European ceramic sector: a systemic review - Applied Thermal Engineering, 2001 - Vol. 21.

Bergaya F., Then B.K.G. and Lagaly C. Handbook of Clay Science - Elsevier, 2006. - Vol. 1.

Christidis G. E. Advances in the Characterization of Industrial Minerals- the European Mineralogical Union and the Mineralogical Society of Great Britain&Ireland, 2011. - Vol. 9.

Commission Européenne Document de référence sur les meilleures techniques - Fabrication des céramiques - 2007.

Commission Européenne Fabrication des céramiques- Document de référence sur les meilleures techniques disponibles- 2007.

Demirkiran A. S., Artir R. and Avci E. Effect of natural zeolite addition on sintering kinetics of porcelain bodies - Journal of Materials Processing Technology. - Elsevier, 2008 - 465-470 : Vol. 203.

G.W. Brindley and G. Brown Crystal Structures of Clay Minerals and Their X-Ray Identification- Mineralogical Society, 1980.

Gastuche M.C., Toussaint F. and Fripat J.J. Study of Intermediate stages in the kaolin -> metakaolin transformation - 1962.

Goleanu, Aurica Achieving Self-Glazed Porcelain Bodies -http://www.ceramicindustry.com. - Ceramic Industry Magazine, 2001 1-octobre
http://www.ceramicindustry.com/articles/achieving-self-glazed-porcelain-bodies.

Iqbal Yaseen and Lee William Edward Microstructural Evolution in Triaxial Porcelain - J. Am. Ceram. Soc, 2000. - 12 : Vol. 83.

Iqbal Yaseen and Lee William Edward Microstructural Evolution in Triaxial Porcelain - J. Am. Ceram. Soc., 2000. - 12 : Vol. 83.

Jeoung-Ah Kim The characterisation of paper-composite porcelain in a green state- Journal of the European Ceramic Society. - Elsevier, 2004 - Vol. 26.

Kivitz E. [et al.] Reduction of the porcelain firing temperature by preparation of the raw materials- SciencesDirect, 2009- Vol. 29.

Lippens B.C. and Boer J.H. De Studied on pores Systems in Catalysts V. The t Method - Journal of Catalysis, 1964. - 319-323 : Vol. 4.

López Simón Yobanny Reyes, Rodríguez Juan Serrato and Sueyoshi Satoshi Sugita Determination of the activation energy for densification of porcelain stoneware - Journal of Ceramic Processing Research, 2011- 3 : Vol. 12.

Martín-Márquez J., Rincón J. Ma. and Romero M. Effect of firing temperature on sintering of porcelain stoneware tiles - Ceramics International. - 2008 - Vol. 34.

Martín-Márquez Jorge, Rincón Jesús Ma. and Romero Maximina Effect of microstructure on mechanical properties of porcelain stoneware - Journal of the European Ceramic Society. - Elsevier, 2010 - 3063-3069 : Vol. 30.

Martín-Márquez Jorge, Rincón Jesús Ma. and Romero Maximina Mullite development on firing in porcelain stoneware bodies - Journal of the European Ceramic Society. - Elsevier, 2010 - Vol. 30.

Norton F.H. elements of ceramics second edition - Massachussetts : Addison-Wesley Publishing Company, 1974.

Rouquerol J. [et al.] Recommendations for the characterization of porous solids - Pure & Appl. Chem., 1994. - 8 : Vol. 66.

Santos Teresa P. [et al.] Porosity characterization of old Portuguese ceramic tiles - Lisboa : Construction and Building Materials, 2011 - Vol. 28.

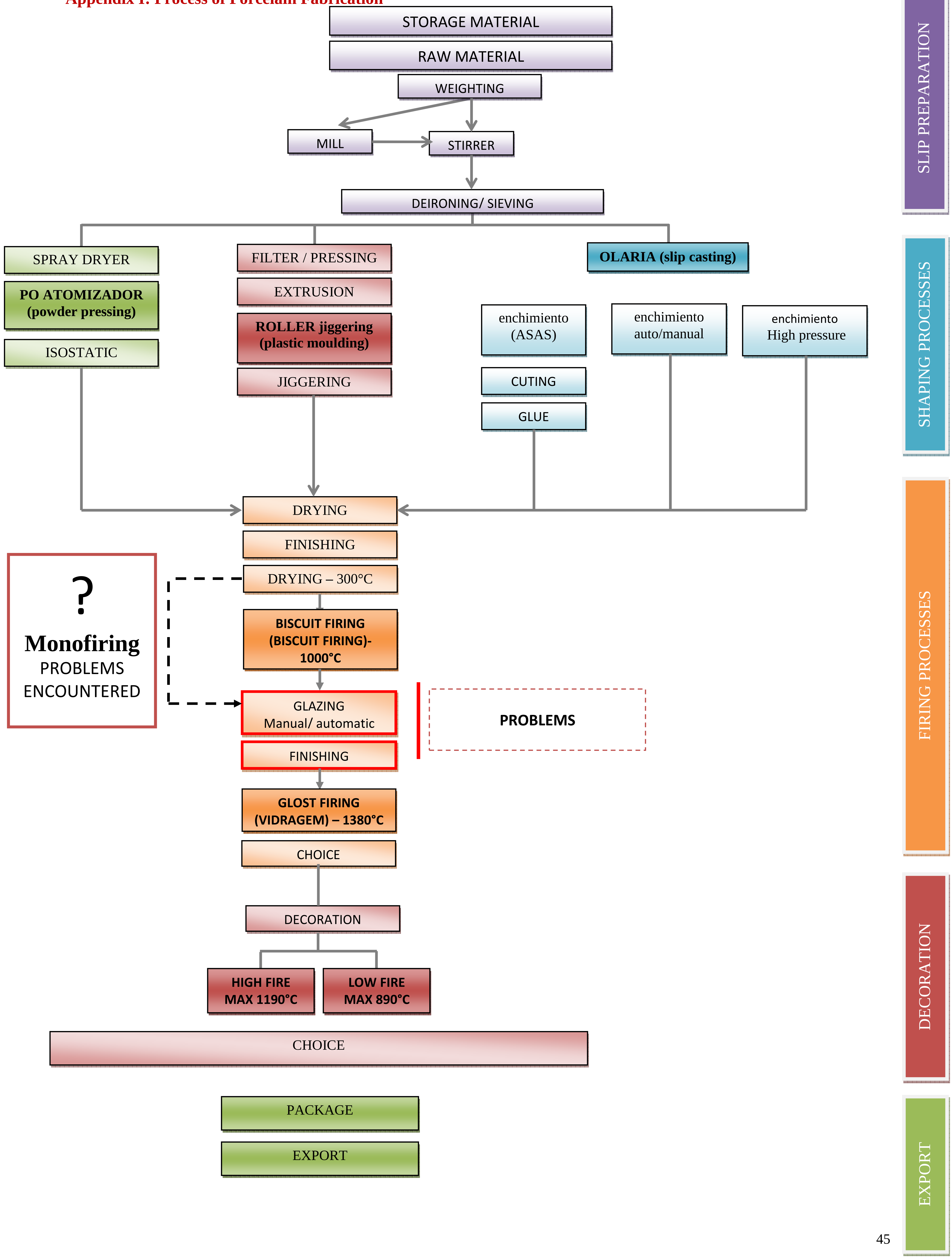
Searle Alfred Broadhead and Grimshaw Rex W. The chemistry and physics of clays and other ceramic materials- Interscience Publishers, 1959.

Storck Sebastian, Bretinger Helmut and Maier Wilhelm F. Characterization of micro- and mesoporous solids by physisorption methods and pore-size analysis- Applied Catalysis, 1998. - Vol. 174.

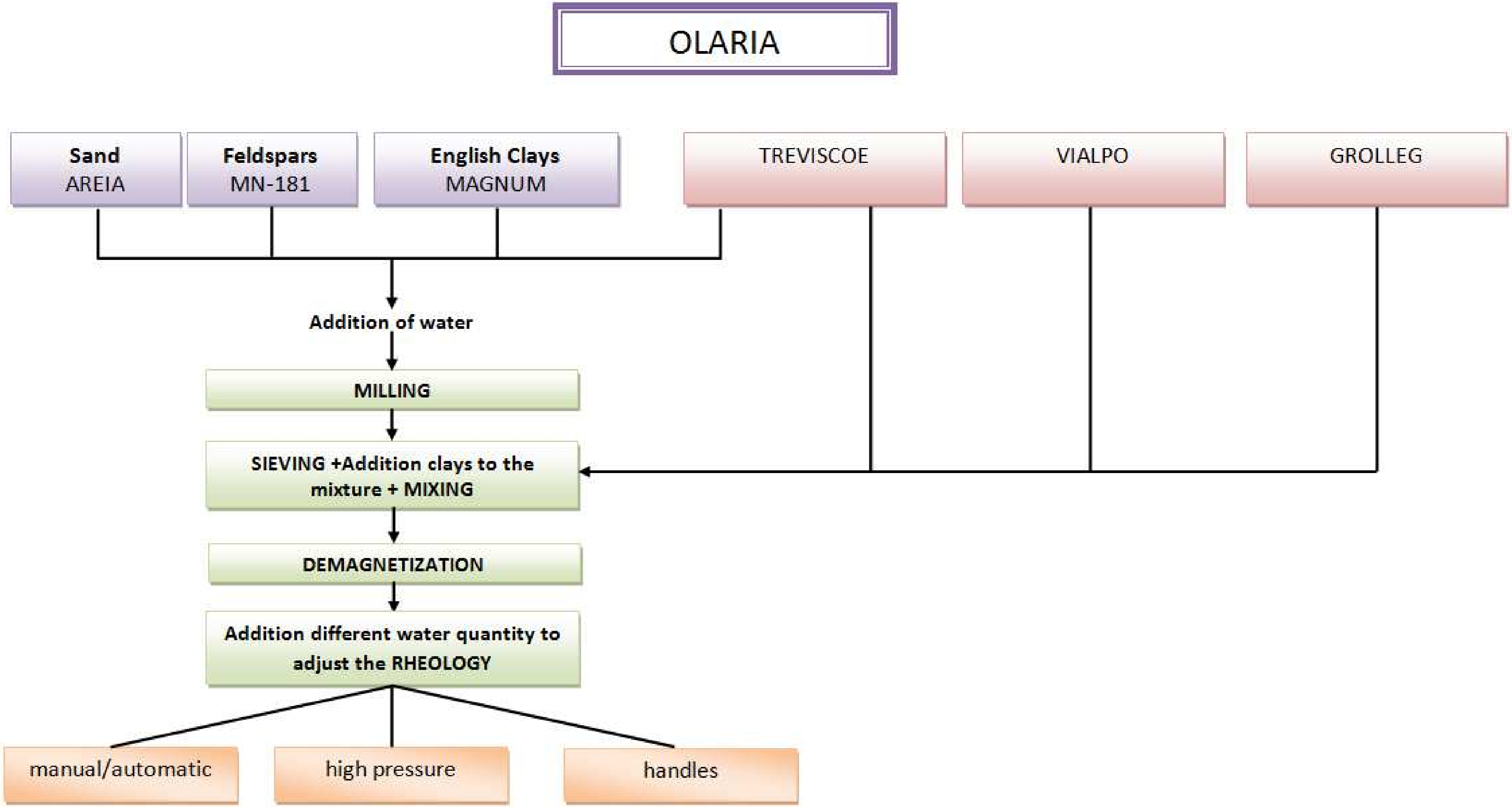
Subbanna Manjunath [et al.] Population balance model for solid state sintering I. Pore shrinkage and densification - 2001 : Ceramics International. - Vol. 27.

Vereshchagin V. I., Mogilevskaya N.V. and Gorbachev D. V. Low fired Porcelain with diopside and marshalite additions - Glass and Ceramics, 2013 - 11-12 : Vol. 69.

Appendix I: Process of Porcelain Fabrication



Appendix II: Process paste liquid production



Appendix III: Process powder and plastic paste production